The Accurate Analysis and Environmental Geochemistry of Inorganic Elements in Peat Bogs

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Abstract

Despite the increasing interest in using peat bogs as archives of atmospheric deposition, the lack hitherto of a common, validated sample preparation method and of a certified peat reference material has hindered not only the quality assurance of the generated analytical data but also the interpretation and comparison of peat core elemental profiles from different laboratories in the international community. The work described in this thesis is primarily concerned with (i) the development of analytical methods for the determination of inorganic elements in peat, (ii) the production and analysis of a certified peat reference material, and (iii) the application of methods and procedures to the generation and interpretation of elemental profiles in cores from the largest ombrotrophic peat bog in Scotland.

The effects of sample preparation on the determination of inorganic elements in peat samples were thoroughly investigated. Four existing sample digestion methods [(USEPA methods 3051 (HNO_3), 3051a (HNO_3/HCl), 3052 (HNO_3/HF), and ISO standard 11466 (HNO_3/HCl)] were used to digest a high-ash Canadian peat material (OGS 1878 P-6) that had not been formally certified. Major and trace elements were determined by ICP-OES. Accurate and precise analytical results were achieved for all elements investigated by USEPA method 3052, while USEPA method 3051 provided acid-extractable contents of satisfactory accuracy except for some major elements (Al, Ti), for which the total digestion method was essential. Two microwave-assisted digestion protocols, namely an adapted USEPA method 3051 for acid-extractable element concentrations and an adapted USEPA method 3052 for total element concentrations, were developed and proposed as standard digestion methods for peat and subsequently used in sample preparation for the determination of elements in a candidate peat reference material originating in Scotland.

Peat for the development of the candidate reference material was collected from Flanders Moss ombrotrophic peat bog in central Scotland in September 2001. The wet peat (70 kg) was air-dried at 30°C and homogenised using facilities at the Macaulay Institute, Aberdeen. After bottling of the dried material (30 g aliquots) and tests to ensure homogeneity, with stability subsequently confirmed after 1, 3, 6 and 12 months, the candidate peat reference material was distributed to 16 laboratories of

international standing, of which 14 from nine countries ultimately participated in an inter-laboratory comparison exercise. Ten laboratories supplied data for acid-extractable (HNO_3, HNO_3/HCl, $HNO_3/HClO_4$) concentrations and seven for total (HNO_3/HF, HNO_3/HBF_4, $HNO_3/H_2O_2/HF$) concentrations, using a range of digestion conditions and a variety of analytical techniques (AAS, ICP-OES, ICP-MS), including, in the case of one laboratory, XRF analysis of the solid phase, and, in two others, thermal decomposition AAS for Hg. After subsequent rigorous statistical tests to reject outliers, the certified or information-only values, as appropriate, for acid-extractable and total Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, P, Pb, S, Ti, V and Zn concentrations were reported. Isotope dilution mass spectrometry was then applied in this laboratory to determine and confirm the total Pb concentration in this low-ash peat reference material, which was designated NIMT/UOE/FM/001 in recognition of the author's home (National Institute of Metrology, Thailand) and host (University of Edinburgh) institutions and the origins of the peat.

The analytical methods and quality assurance procedures developed using the certified reference material were applied to the analysis of two Flanders Moss peat cores that had been collected by different coring techniques. An offset between the elemental profiles of the two cores was attributed to loss of surface material in the case of one, confirmed by stable ($^{206}Pb/^{207}Pb$) and radioactive (^{210}Pb) isotopic analysis. The depth profiles of the various elements were interpreted in terms of influences such as nutrient uptake and recycling, anthropogenic inputs from industry, energy generation and transport, soil dust, and post-depositional remobilisation and redistribution. For Pb, for which a record of atmospheric deposition was retained, the relative contributions of different sources (e.g. smelting, coal combustion, car-exhaust emissions) during the industrial era were assessed using Pb concentration and $^{206}Pb/^{207}Pb$ ratio variations in ^{210}Pb-dated peat. The importance of atmospheric Pb deposition prior to the introduction of leaded petrol was confirmed and, in the more distant past, a small Pb peak at a depth of ~1 m was tentatively attributed to Pb mining and smelting activities during the period of the Roman Empire.

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Chapter 1

Introductory Overview

Environmental samples such as tree rings, mosses, aquatic sediments, snow, ice, and peat have been used as archives for the study of atmospheric metal deposition (Sheppard and Funk, 1975; Rühling and Tyler, 1984; Norton and Kahl, 1987; Farmer, 1991; Eklund, 1995; Boutron *et al.*, 1994, 1995; Shotyk, 1996; Shotyk *et al.*, 2000; Van de Velde *et al.*, 1999, 2000; Veysseyre *et al.*, 2001). The surface layers in ombrotrophic raised peat bogs are isolated from the influence of local ground water and surface water, and receive their inorganic content by atmospheric deposition only (Lindsay, 1995; Shotyk, 1996). Ombrotrophic peat that has accumulated during the past hundreds or thousands of years, therefore, can be used to study vegetation history, climate change, and, in principle, the historical trend of atmospheric metal deposition. Most recent relevant research results (Espi *et al.*, 1997, Shotyk, 1996, 1997; Farmer *et al.*, 1997a; MacKenzie *et al.*, 1997, 1998; Steinmann and Shotyk, 1997; Shotyk *et al.*, 1998, 2000; Weiss *et al.*, 1997, 1999), e.g. for Pb, have been consistent with information from other archives, including lake sediments and ice cores, and are compatible with known historical trends where available, e.g. the emission of Pb from different sources. Given the increase in this type of study, however, the lack of a common, validated sample preparation method and of a certified peat reference material has hindered not only the quality assurance of the generated analytical data but also the interpretation and comparison of peat core metal profiles from different laboratories in the international community. Instead of using an authentic peat reference material, quality control in this sort of study has long been referred to certified reference materials (CRMs) developed for plants and soils. Although an attempt, as yet uncompleted, was made to develop a peat reference material for quality control use by laboratories in the international peat bog community (Barbante *et al.*, 2000), the material was of fen origin and had high ash content (~ 20%), uncharacteristic of ombrotrophic peat bogs. In addition, different laboratories in this field of research currently adopt a wide range of practices, including the determination of acid-extractable and of total elemental concentrations by various instrumental analytical techniques. To compare and standardise these different approaches, there has been a growing need to develop a new candidate peat reference material, derived

from an ombrotrophic bog, and to subject it to an international inter-laboratory study as part of the certification process. The primary aim of this project, therefore, was to develop a peat bog candidate reference material, to be characterised for different preparative digestion methods. Reference materials characterised for both acid-extractable and total concentrations of elements are of value to laboratories that cannot or do not employ HF to achieve total dissolution of aluminosilicate minerals in sample matrices. The peat bog candidate reference material so developed could then be used as a quality control in the study of atmospheric metal deposition via application to the determination of vertical profiles of inorganic elements in peat bog cores. The structure of this thesis is as follows.

Chapter 2 reviews the literature relevant to this research project. General aspects of peat bogs, previous research on the use of peat bogs as archives of atmospheric metal deposition, questions concerning the validity of peat bogs as archives of atmospheric metal deposition, the effects of sample preparation on the determination of elemental concentration in peat, and the general requirements in the preparation of certified reference materials are described and discussed, leading to a statement of the specific objectives of the research presented in this thesis.

Chapter 3 contains a comparative study of four digestion methods for preparation of peat material for analysis by ICP-OES: conventional HNO_3 digestion, the adapted USEPA method 3051a (HNO_3/HCl), the adapted USEPA method 3052 (HNO_3/HF), and the standard aqua regia (HNO_3/HCl) extraction procedure according to ISO standard 11466, applied to peat and some other matrices. A case study of two digestion methods for total and acid-extractable elemental concentrations in peat from a Flanders Moss peat core collected in 1999 is also presented in this chapter.

Chapter 4 focuses on the development of the ombrotrophic peat bog reference material. Starting from collection of fresh peat material to certification of the reference material, this chapter provides details of the entire process. It can be divided into five parts; initial preparation of the candidate ombrotrophic peat bog reference material, preliminary homogeneity study of the bulk candidate material, homogeneity testing of the candidate material, stability testing of the candidate material, and

characterisation and certification of the candidate ombrotrophic peat bog reference material by an international inter-laboratory exercise.

Chapter 5 presents the application (using ICP-MS) of isotope dilution mass spectrometry (IDMS), the primary method of measurement, to the determination of Pb concentration in the ombrotrophic peat reference material developed in this project. This chapter can be divided into two major parts; first IDMS on sample digest solution, and then on the solid peat material in the second part.

Chapter 6 describes and interprets elemental concentration profiles determined for a core collected from the Flanders Moss peat bog in 2001, with analytical quality assurance provided by the certified reference material developed in this project. Comparisons are drawn with results, including Pb isotopic data, for a Flanders Moss peat core collected by a different coring method in 1999.

Chapter 2
A Critical Review of the Use of Peat Bogs as Archives of Atmospheric Metal Deposition

Although peat cores from many sites around the globe have been used to reconstruct present and past rates of atmospheric metal deposition, there are still problems with regard to the appropriateness of methods for sampling and analysis. Also, the use of enrichment factors for normalising element concentrations to the average composition of the Earth's crust has recently been questioned. This chapter reviews the literature as follows: general aspects of peat bogs, previous researches on the use of peat bogs as archives of atmospheric metal deposition, questions concerning the validity of peat bogs as archives of atmospheric metal deposition, the effects of sample preparation on the determination of elemental concentration in peat, and general requirements in the preparation of certified reference materials. Finally, the specific objectives of this research will be outlined.

2.1 General aspects of peat bogs

Peat is a soil that is made up of the partially decomposed remains of dead plants which have accumulated on top of each other in waterlogged places for thousands of years. Peat is brownish-black in colour and in its natural state is composed of 90% water and 10% solid material. It consists of *Sphagnum* moss along with the roots, leaves, flowers and seeds of heathers, grasses and sedges. Occasionally the trunks and roots of trees such as Scots pine, oak, birch and yew are also present in the peat. Areas where peat accumulates are called peatlands.

Peatlands are wetlands ecosystems that are characterised by the accumulation of organic matter, which is produced and deposited at a greater rate than it is decomposed, leading to the formation of peat. Peatlands are different from non-peat forming wetlands by virtue of interrelated hydrological, chemical, and biotic factors that result in a decrease in decomposition relative to plant production, allowing for the accumulation of peat. The initiation of peat accumulation is related to stabilisation of seasonal water levels and restriction of water flow through a wetland, in conjunction with leaching of salts from the mineral substrate, which allows for the establishment and development of a moss layer. The establishment of a moss layer results in the

accumulation and maintenance of nutrients in a non-available form, reducing vascular plant production. Stabilised water levels, anaerobic conditions, and decreased nutrient availability lead to a substantial decrease in decomposition rates, that result in the development of peat accumulating ecosystems (Lindsay, 1995). As peat accumulates, surface vegetation can become isolated from the underlying substrate; coupled with biological and chemical processes this can lead to acidification and oligotrophication. Peatlands are classified into geogenous fens and ombrogenous bogs, each with distinctive indicator species, acidity, alkalinity, and base cation content.

2.1.1 Fens or drier swamps

Fens or drier swamps are geogenous ecosystems that are affected by mineral soil waters (ground and/or surface) that may be relatively rich in mineral elements. Fens can be subdivided on the basis of hydrology into: *soligenous*, largely influenced by flowing surface water; *topogenous,* largely influenced by stagnant ground water; *limnogeneous,* largely influenced by associated lakes and ponds. All three types of fens have water levels at or near the peat surface. *Soligenous fens* commonly have discrete patterns of open pools alternating with elongate, shrubby to wooded ridges (strings) oriented perpendicular to the direction of surface water flow. These patterned fens may be either acidic or basic. *Topogenous fen* complexes are characterised by a high and relatively stagnant water table dependent on the shape of the topography allowing the accumulation of a ground peat surface that is level or imperceptibly sloping and where there is little or very impeded lateral water movement. Topogenous, limnogenous, and some soligenous fens are non-patterned.

2.1.2 Bogs

Bogs are ombrogenous peatlands that receive their surface water only from precipitation and have low water flow. The water table is generally 40-60 cm below the peat surface. In these situations the high stagnant water table and the accumulation of peat do not depend on the concentration of drainage into a topographic hollow or into a drainage line so much, but rather on a high precipitation input and a low evapo-transpiration loss. Because the only source of water is from the atmosphere, such habitats are termed "ombrogenous" and are of consistently low base status as they are dependent for the most part on the ionic content of rain water.

Peat type changes from fen to bog peat when the growing peat surfaces in the centre of such mires are raised to a level where they are isolated from any nutritional effect of soil water draining into the site, when their nutrition becomes dependent on rainwater and acidification of the environment ensues, reducing their decomposition rates, while increasing peat accumulation. The result is that the centre of the peat surface grows faster than the margins, which remain influenced by oxygenated moving soil water and hence by faster decomposition rates. These margins then form a 'steep' slope separating a domed bog plane from a marginal 'lagg' depression - hence the phrase "raised bog". Although the transition from fen to bog peat is associated with natural development of the vegetation succession, in the post-glacial period this change in peat stratigraphy at many sites seems to have been correlated with climatic deterioration and a wetter peat surface, thereby encouraging renewed upward growth.

Bogs are dominated by oligotrophic species of *Sphagnum* (see Figure 2.1); feather mosses: *Pleurozium schreberi* and *Hylocomium splendens*; and lichens of *Cladonia* and *Cladina*. They may be open, wooded or forested with trees limited to *Picea mariana*. As a result of the low thermal conductivity of dry *Sphagnum*, bogs have lower surface water temperatures than other surrounding organic and non-organic soils. Permafrost is consequently restricted to bogs at its southern limit, where it forms peat plateaus (Lindsay, 1995).

Figure 2.1 Structure of a *Sphagnum* Plant. Attached to the stem are two types of branches. The spreading branches stick out and give the plant structure. The hanging branches are pressed to the stem and help to draw up water (Lindsay, 1995).

Although the categories of wetland community are mainly determined by the hydrology of the site, a major contributing factor is the nutritional status of the site, and particularly of the water influencing the site. This influence is recognised by the

use of the term "ombrotrophic" nutrition to denote those situations where such nutrition is dominantly rainwater, and "minerotrophic" where mainly soil/substrate water nutrition occurs. The term "ombrotrophic" is derived from "ombros" (Greek) meaning rain shower, and "trophe" meaning nourishment. Rainwater nutrition is of course always base-deficient or "oligotrophic", whereas soil water nutrition is very variable depending on the influence of the geology and other characteristics of the catchment from which drainage water is derived. Accordingly it may be "oligotrophic", "mesotrophic", or "eutrophic", meaning poorly, average or well nourished, respectively.

2.1.3 Formation of peat bogs

There are two major paths of peat bog formation as identified by Sjors in 1983 (Lindsay, 1995): *terrestrialisation* and *paludification*. *Terrestrialisation* is the process in which a shallow lake becomes overgrown by fen vegetation, steadily filled with fen peat and then overwhelmed by a rising mound of rain-fed bog peat. *Paludification* represents the process by which peat forms directly over a soil or rock surface under cold and humid climatic conditions, and may not involve any fen precursor prior to bog development. However, in both *terrestrialisation* and *paludification*, the vegetation's roots cannot penetrate through the peat layers to obtain nutrients in ground water. The classic description of bog development is that of the simple raised dome formed by *terrestrialisation* (see Figure 2.2). Other bog types, particularly blanket bog, may show a different sequence of development, but most of the basic principles of water-logging, peat accumulation and hydrological balance are common to all.

Many raised bogs began life as a shallow basin formed in relatively impermeable glacial clays. After being flooded by groundwater in early post-glacial times, the basin became a lake with a fringe of fen vegetation. In 2000 years time, the lake became overgrown by fen plants. These fen plant remains did not decay completely and then accumulated, filling the basin with fen peat and trapped sediment. Once the basin was entirely full, the plants at the centre were largely cut off from solutes either from the basal sediments or from the lake margins. Such conditions are intolerable to most plant species except the genus *Sphagnum*, with the result that bog moss carpets came to dominate vegetation as shown in Figure 2. 3 (Lindsay, 1995).

Sphagnum is more resistant to decay than the majority of plant material because much of its chemical composition is resistant to decomposer microbes. Steady accumulation of dead *Sphagnum* and the litter of other bog species are not matched by the overall rate of decay, causing the lining layer to be gradually raised above the surrounding geotropic fen by up to 2 mm per year. After 5,000-7,000 years of such accumulation, the central parts may rise more than 10 m above the geographic fen deposits, which are completely smothered beneath a single great mound of undecayed peat (Lindsay, 1995).

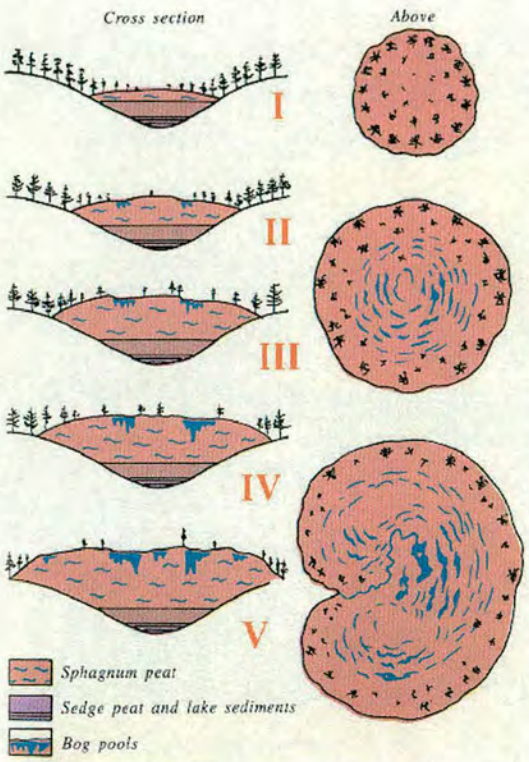


Figure 2.2 Formation of raised bog:
(I) Centrally thinned wooded bog or open fen, surrounded by a bog pine forest;
(II) Centrally bare (treeless) raised bog with beginnings of bog hollows;
(III) Concentric rings consisting of hollows and hummock ridges, standing water forms pools in hollows, marginal pine forest;
(IV) Narrow bog pools surrounding irregular hollows and small lakes in the centre;
(V) Outlet stream divides bog in two (or more) lobes that continue to develop into a complex mire. (Masing, 1997)

Figure 2.3 Carpets of *Sphagnum* plants form the building blocks of most peat bogs (Lindsay, 1995).

The other component which is dominant in the bog system is the characteristic acidity of the bog environment. This is due to ion exchange processes between the bog waters and the lining vegetation. In these systems, the few cations available are taken into the plant and exchanged for hydrogen ions. With few metal cations to provide buffering, carbon dioxide dissolves into a solution of carbonic acid to give bog pore-waters of around pH 4. A wide range of complex humic acids may also contribute in varying amounts to this acidity (Lindsay, 1995).

2.1.4 Raised bogs

A raised bog is a bog that takes the shape of a relatively simple dome. It forms under a range of conditions from strongly oceanic to relatively dry continental climates, and is widespread in boreal regions. It began to form only at the end of the Ice Age about 10,000 years ago. When the land surface was new, the glacial moraine left behind created a hummocky and chaotic plain, which had poor drainage as a consequence. The depressions filled with water, creating thousands of tiny lakes. Over the 10 intervening millennia, these tiny lakes have become the raised bogs. Many overlie sites of shallow glacial lakes, which, filled and occupied by fen and under the influence of the climate, subsequently continued to develop into the classic dome of a raised bog. Raised bog types therefore generally contain evidence of earlier geotrophic phases within their stratigraphic record.

An intact raised bog usually has a gently domed profile with peat depths greatest beneath the mire expanse then decreasing gradually towards the margins. It overlies at least some geotropic fen peat, usually in the deepest parts of the bog. The edges are marked by a steeper *rand* (sloping mire margin), and sometimes bounded by a geogenous fen.

2.1.5 Blanket bog

The other major morphological type of bog is *blanket bog*, a peat formation which always occurs under the cool, and intensely oceanic, climate (Lindsay, 1995). They are called blanket bogs because, from a distance, they appear homogeneous and they hug the topography like a blanket. The tendency to conditions of soil water-logging favourable to *Sphagnum* growth and peat formation (paludification) in such areas

means that bog development has not been confined to level terrain or basins, but occurs as the more steeply sloping ground. Blanket bog has a much more complex topography than raised bog because of the more varied conditions under which it develops. It may change suddenly at a mire margin formed by a rock face or grade imperceptibly into the vegetation of drier mineral soils through a transition of wet heath or grassland.

Blanket bog began life through a combination of both paludification and terrestrialisation. Basins in the topography undergo terrestrialisation and eventually form raised domes of peat, but under a typical climate of blanket bog the process of paludification is capable of covering gentle slopes and plateaux with peat as quickly as the adjoining basins develop domed bogs. In cases where the convex shape is derived purely from peat formation, the unit can be classified as the *unconfined* or *Atlantic raised bog*. The significantly harsher and wetter conditions typical of blanket bog regions mean that such domed elements are generally very different from lowland raised bog in character. They have a more humified peat, a distinctive hydrological budget, and a species complement indistinguishable from the surrounding blanket bog. The entire complement of hydrological units which makes up the peat covered landscape should therefore be regarded as sub-units of blanket mire.

There are five major mire units representing the 'building blocks' within blanket bog complexes: *watershed, valleyside, spur, saddle (eccentric) and intermediate mires* (among bog types). These components are non-peatland features including wet heath and grassland, dry heath and grassland, streams and rivers, and rock outcrops. Separate units are defined on the basis of hydro-morphology and topography. They may merge across areas of thin peat, but generally consist of deeper peat occupying distinct topographic positions within the landform. Features typical of blanket bog compared with those of undisturbed raised bog are summarised in Table 2.1 (Lindsay, 1995).

Table 2.1 Features typical of blanket bog and undisturbed raised bog (Lindsay, 1995).

Blanket bog	Undisturbed raised bog
- the peat being generally ombrotrophic;	- a single dome of ombrotrophic peat
- the landscape being cloaked with peat, with non-peat areas representing isolated islands or corridors – particularly evident from soil maps	- the domes, or complex of domes, generally lying within a non-peat landscape (usually agriculture)
- significant parts having clearly formed through paludification rather than terrestrialisation – particularly evident on slopes	- the dome overlying a greater or lesser extent of fen peat deposits, having developed at least in part by terrestrialisation
- the shape of the peat units in most cases being derived at least in part from the shape of the underlying terrain	- the dome being produced entirely by peat growth and owing little or nothing to the underlying terrain
- separate hydrological units can be identified, but many being directly fused with others, rather than being invariably separated by lagg streams	- at the margins the bog water table linking with the ground water table; the mixed hydrology gives rise to fen (lagg fen) which may surround the dome of peat
- widespread presence of erosion features, the peat thickness varying from only a few centimetres to 7-8 m	- the dome tending towards a half-ellipse in vertical section, with the margin (rand) showing a more pronounced gradient than the centre

2.2 Utilisation of peat bogs as archives of atmospheric metal deposition

It has been proven that the surface layers in ombrotrophic raised bogs are hydrologically isolated from the influence of local ground water and surface water and receive their inorganic content by atmospheric deposition (Shotyk, 1996). The anaerobic and acidic conditions of the bog system retard the rate of decomposition of organic materials, allowing plants and animals to remain preserved in peat profiles for millennia. Bogs that have remained undisturbed in this condition for the past hundreds or thousands of years can be used to study vegetation history, climate change and metal pollution. More recently, they have been used as archives to reconstruct the historical trend of atmospheric metal deposition. Another reason for using peat bogs as archives of atmospheric metal deposition is that peatlands (mires) are widely distributed across the world, accounting for 5% of the land area of the Earth. This offers a good opportunity to study the changing rates of atmospheric deposition on a global basis (Shotyk, 1996). Furthermore, most recent research has yielded results

consistent with information from other archives, e.g. lake sediments and ice cores, and is compatible with known historical trends in the use of Pb (Shotyk, 1996, 1997; Steinmann and Shotyk, 1997). There have also been a number of studies trying to use concentration profiles of Pb and other contaminant metals in ^{210}Pb-dated ombrotrophic peat cores to reconstruct the historical trends in atmospheric deposition (Shotyk, 1996, 1997; Farmer *et al.,* 1997b; MacKenzie *et al.*, 1997, 1998; Steinmann and Shotyk, 1997; Shotyk *et al.,* 1998, 2000; Weiss *et al.,* 1999). The results of these studies are relatively well established and correspond with the information gathered from lake sediment studies and with the historical trends in the use of Pb (Bellis *et al.*, 2002; Farmer *et al.*, 2002).

The utilisation of peat bogs as archives of atmospheric metal deposition has been reviewed by Shotyk (1996). Two *Sphagnum* bogs in the Jura Mountains of Switzerland, La Tourbeire de Genevez and Etang de la Gruyere, were used as examples for distinguishing ombrotrophic from minerotrophic peat by using the Ca/Mg molar ratio in pore waters. This work suggested that ombrotrophic bogs are appropriate for the investigation of atmospheric metal deposition, while it is inadvisable to use minerotrophic peat in this kind of study. In this review, Shotyk suggested a need to correct the natural variations in metal concentrations for changes in peat density and mineral metal contents by normalising the Pb concentrations to scandium (Sc), because of the pronounced variations in bulk density and ash contents in the peat profiles. This correction factor is known as the "enrichment factor, (EF)" and was subsequently used by Shotyk in his other papers. This work concluded that the Etang de la Gruyere is ombrotrophic peat, representing 2100 years of peat accumulation, while the La Tourbeire de Genevez contained a thin layer (20 cm) of ombrotrophic peat, representing less than 50 years of peat formation. The findings showed that the lowest rates of atmospheric Pb deposition during the past 2100 years were 10 times higher than the natural flux. Moreover, the results indicated that the rates of atmospheric Pb deposition in the Jura Mountains of Switzerland had been affected by human activity throughout the past 2100 years. However, additional accurate analyses and dating were required for a more detailed chronology. Shotyk also extended his studies to the atmospheric metal deposition in an oceanic peat bog profile in northern Scotland (Shotyk, 1997). His results indicated that the major (Si,

Ai, Fe, Na, K, Ms, and Ca) and some trace elements (Rb, Sr, Cl, Br, and S) were supplied to the oceanic blanket bogs by two main atmospheric sources: mineral aerosols from weathering of crustal rocks and sea salt spray. His studies revealed that 91.5-99% of the major elements and trace elements supplied to the bogs by rainwater were not retained by the peat. Thus, depth profiles of these elements in the peat cannot be used as a quantitative indicator of sea salt inputs to the bogs (Shotyk, 1997).

Shotyk *et al.* (1996) reported a significant degree of enrichment of As, Sb, and Pb in Roman times. This indicated that the anthropogenic fluxes of these metals have exceeded the natural fluxes for more than 2000 years. The isotopic composition of Pb provided no evidence of vertical downward Pb migration, suggesting that the bog had clearly preserved the historical record of atmospheric Pb deposition. Age dating using ^{210}Pb (verified independently by pollen markers) indicated the chronology of changing metal concentrations during the past 150 years.

Steinmann and Shotyk (1997) studied mass balances in two *Sphagnum* peat bogs from the same Jura Mountain region. This study used Sc as a conservative tracer to distinguish between the primary sources of major elements to the bogs. The results indicated that Sc can be used to distinguish bog type, and were in good agreement with other methods. This finding reported that quartz, feldspar, and muscovite are the main mineral components of the ash. Biogenic Si represents another important fraction of ash and is abundant at discrete depths. The vertical peat core profiles showed no significant changes in mineralogy with depth. This suggests that the fine-grained silicates supplied by soil dust have not been measurably weathered during the past two millennia.

Another study of the history of atmospheric Pb deposition since 12,370 ^{14}C yr BP from a peat bog, Jura Mountains, Switzerland, was conducted by Shotyk *et al.* (1998). The $^{206}Pb/^{207}Pb$ ratio and the Pb enrichment factor (Pb EF) were used to distinguish natural sources from anthropogenic sources of atmospheric Pb. Both the $^{206}Pb/^{207}Pb$ ratio and the Pb enrichment factor showed a similar trend of atmospheric Pb deposition. The $^{206}Pb/^{207}Pb$ profile indicated that until 3,000 ^{14}C yr BP, soil dust was

the main source of Pb supplied to the bog. The decline in $^{206}Pb/^{207}Pb$ ratio and the increase in Pb EF starting at 3,000 ^{14}C yr BP indicated that anthropogenic sources have dominated atmospheric Pb emissions in Europe ever since (Figs. 2.4 - 2.5). It was suggested that these data can be explained by historical records of ancient Pb mining at the beginning of the Roman Period (3000 ^{14}C yr BP – 1010 ^{14}C yr BP). Above 32 cm in the peat profile (dated A.D. 1879), the Pb enrichment factor increased rapidly and the sharp decrease in the $^{206}Pb/^{207}Pb$ ratio corresponded to the history of Pb use. This period coincided with the Industrial Revolution in Europe, which introduced great advances in smelting techniques and increased Pb production. The most rapid rise in Pb enrichment factor (and the most rapidly decreasing $^{206}Pb/^{207}Pb$ ratios) from 1930 to 1979 were attributed to the introduction of gasoline Pb into Switzerland in 1947. Subsequently, the decrease in Pb enrichment was attributed to the introduction of unleaded gasoline. These findings were broadly in agreement with the Greenland GRIP ice core Pb record for the past three millennia (Hong *et al.*, 1994). Moreover, the peat bog record was consistent with the recent changes in Pb concentrations seen in Greenland snow (Candelone *et al.*, 1995).

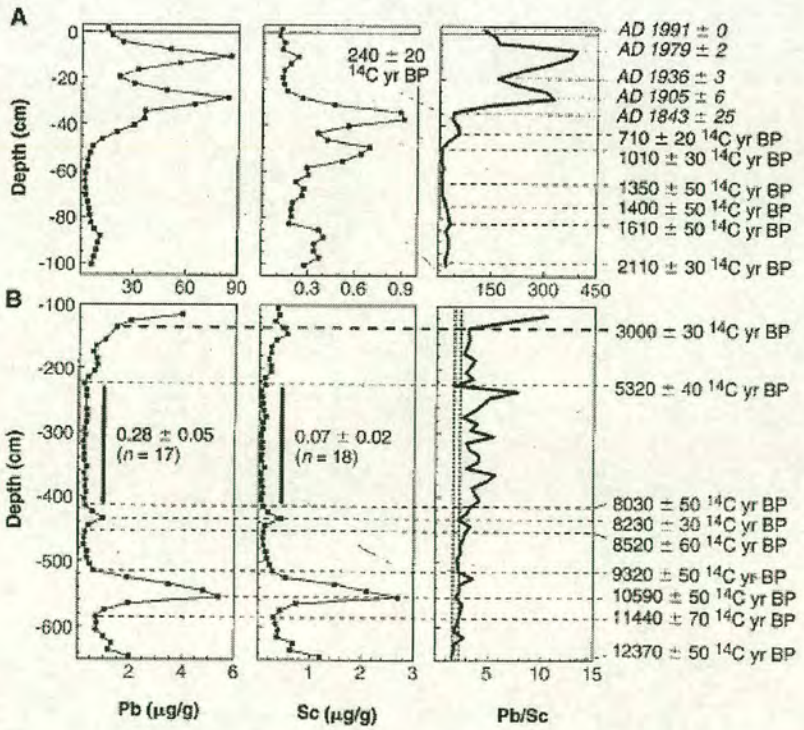


Figure 2.4 Pb and Sc concentration (µg/g) and Pb/Sc ratios in peat cores from Jura Mountains, Switzerland (Shotyk *et al.*, 1998).

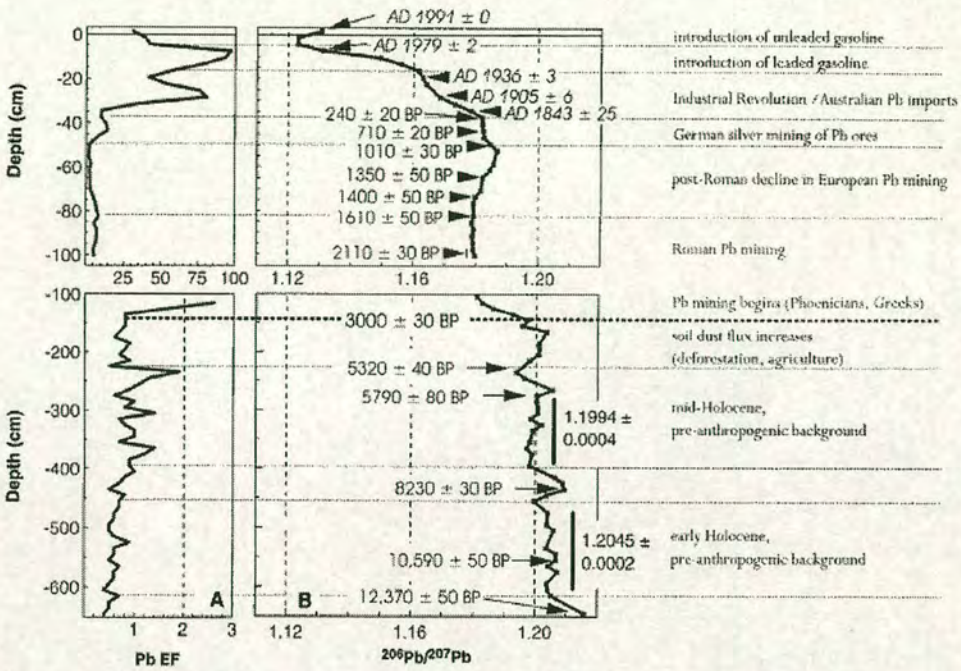


Figure 2.5 $^{206}Pb/^{207}Pb$ ratios in peat cores from Jura Mountains, Switzerland (Shotyk *et al.*, 1998).

Further study of atmospheric Pb deposition since the Industrial Revolution was conducted in western, central, and southern Switzerland by Weiss *et al.* (1999). Five rural peat bogs were used. They found that, between 1880 and 1920, Pb enrichment had increased by 40 to 80 times, and between 1900 and 1980 enrichments ranged from 80 to 100 times. Their results indicated the increase of anthropogenic Pb in all five cores between the Industrial Revolution and 1985, because of the replacement of coal by oil after ca. 1920, the use of Australian Pb in industry, and the extensive combustion of leaded gasoline after 1950. The results also demonstrated that the introduction of unleaded gasoline in 1985 had a large effect on Pb deposition in all five cores. The Pb enrichment dropped by a factor of two to four. The study provided strong evidence that the chronological record of atmospheric Pb deposition derived from the peat cores was consistent with the historical use of Pb.

Another study of atmospheric Pb deposition in Switzerland was conducted by Shotyk *et al.* (2000). Eight peat cores from different Swiss peatland sites were used to calculate inventories of anthropogenic Pb. In this study, Sc and Zr were used as reference elements to calculate Pb enrichment factors. The shapes of the Pb/Sc and Pb/Zr profiles suggested that Pb had been supplied by atmospheric deposition at all

sites. They also used the cumulative, anthropogenic, atmospheric Pb (CAAPb) factor to calculate an inventory of total anthropogenic Pb per unit area of the bog surface. Shotyk *et al.* (2000) also claimed that this approach was simple and robust, and independent of the rate of peat accumulation. Furthermore, the assumptions about the immobility of Pb and the age dating of peat profiles were not needed. It was pointed out that with this approach it should be possible to undertake continental and global inventories of atmospheric metal deposition for both the natural and anthropogenic component of most trace metals of environmental interest.

Novak *et al.* (2003) studied the origin of Pb in peat cores from Central Europe. They reported that peat from the region of the Czech Republic dated at 11,000 year B.P. had a high $^{206}Pb/^{207}Pb$ ratio, while peat deposited around 1800 A.D. had a lower ratio, which indicated that environmental Pb in Central Europe had been affected by human activity before the beginning of the Industrial Revolution. The production of Ag-Pb, coal, and leaded gasoline peaked in 1900, 1980, and 1980, respectively. In contrast to other European countries, no peak in annual Pb accumulation rates was found in 1900 in their work. The highest annual Pb accumulation rates in peat were consistent with the highest Pb emission rates from coal-fired power plants and traffic (1980). A considerably higher proportion of coal emissions, relative to gasoline emissions, was responsible for the higher $^{206}Pb/^{207}Pb$ ratios in the recent atmosphere of Central Europe compared with that of Western Europe. As in Western European countries, the gasoline sold in the Czech Republic during the Communist era (1948 - 1989) contained an admixture of low-radiogenic Precambrian lead from Australia.

Meanwhile, a study carried out in English peat bogs reported that the $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{207}Pb$ data indicated that English ores were the predominant sources of Pb-deposited during the pre-Roman, Roman, and Medieval Periods in England (Le Roux *et al.*, 2004).

Recently, work on peat bogs has been extended to the atmospheric deposition of Hg and rare earth elements. Krachler *et al.* (2003) reported that a peat core from a Swiss bog provided a record of atmospheric rare earth element (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) deposition. Concentration profiles obtained for all rare earth elements were almost identical, except for Ce and Eu. Calculation of

enrichment factors (EF) revealed a distinct depletion of heavy rare earth elements relative to light rare earth elements in peat samples since the beginning of the 19th century, which marks the onset of the Industrial Revolution in Europe, suggesting a pronounced influence by anthropogenic activities. Enrichments of rare earth element calculated using Sc as a reference element exceeded unity, relative to the Upper Continental Crust. Overall, values of EF in all peat samples ranged from 1.96 for Sm to 2.34 for Gd, with considerably lower values of EF for Ce (1.82) and Eu (1.44), respectively. It was reported that a significant enrichment of all rare earth elements, which may have been caused by military activities, were observed in the peat section dating from World War II. The concentration profiles of rare earth elements were similar but not identical to those of other lithogenic, conservative reference elements such as Sc, Y, Al, Zr and Ti.

Givelet *et al.* (2003) studied the record of atmospheric Hg accumulation since pre-industrial times in peat cores from southern Ontario. The mercury accumulation rates were separated into "natural" and "excess" components by comparing the Hg/Br ratios of modern samples with the long-term, pre-anthropogenic average Hg/Br. They reported that the beginning of Hg contamination from anthropogenic sources dated from AD 1475. During the late 17th and 18th centuries, deposition of anthropogenic Hg was at least equal to that of Hg from natural sources. Anthropogenic inputs of Hg to the bogs have dominated continuously since the beginning of the 19th century. Accurate age dating of recent peat samples showed that the maximum rate of atmospheric Hg accumulation occurred between AD 1956 and 1959. They reported that the Hg concentration profiles resemble those of Pb, an element which is known to be immobile in peat bogs. They suggested that the correlation between these two metals indicated that the predominant anthropogenic source of Hg (and Pb) was coal burning. They found that Hg deposition rates today still exceed the average natural background values by 7 to 13 times.

Shotyk and Krachler (2004) studied and reconstructed a chronological atmospheric deposition of Ag and Tl in Switzerland. The lack of enrichment of Ag and Tl in the basal peat layer shows that mineral dissolution in the underlying sediments has not contributed measurably to the Ag and Tl inventories in the peat column, and that Ag and Tl were supplied by atmospheric deposition. Ag and Tl are considered immobile

because the temporal and spatial peak distribution in Ag and Tl concentrations are similar to those of Pb, which is known to be immobile in peat profiles. Ag showed a high enrichment and variation in concentration. Holocene climate change and land use history resulted in variation of Ag concentrations and enrichment factors (EF) in ancient peat. High Ag enrichment may be due to weathering phenomena or biological processes, both of which are driven by climate. They suggested that the "natural background" EF of Tl in ancient peat is close to unity, indicating a lack of significant enrichment of this element in atmospheric aerosols from chemical weathering of crustal rocks. They reported that the enrichments of Ag and Tl in modern peat from the Industrial Period are at least an order of magnitude greater than values for the ancient peat.

The common use of enrichment factors by many authors is considered to be dubious by others (Reimann and De Caritat, 2000). There are many possible problems regarding enrichment factors, for example; the difference in composition of the earth's crust at any given location compared with that of the global average crust, and fractionation processes of elements during their transfer from the crust to the atmosphere, such as winnowing or weathering. It is considered strange that enrichment factors of the same elements always show a high value regardless of where the samples were taken, even though there are a lot of variations in geogenic element levels and the different element concentrations emitted from different sources of pollution. In the study of "Intrinsic Flaws of Element Enrichment Factors (EFs) in Environmental Geochemistry" conducted by Reimann and De Caritat (2000), they recommended that the indiscriminate usage of enrichment factors in geochemical data should be abandoned. They showed data which indicated that enrichment factors did not provide a simple technique to distinguish between anthropogenic and geogenic element sources or to quantify anthropogenic interference relative to natural element fluxes. They advised that, instead of using enrichment factors, it is better to study the raw data, which are collected from several different compartments of the ecosystem over a large enough area to allow meaningful comparison. This provides a good opportunity for understanding the interactions between atmosphere, biosphere, hydrosphere, and pedosphere – and the human interference with element cycles on both local and regional scales. They also pointed out that the major advantage of

using raw data is that they are not affected by an interfering second element that may show locally high or low concentration for many different reasons.

2.3 Questions concerning the validity of peat bogs as archives of atmospheric metal deposition

In 1996, a workshop on "Peat Bog Archives of Atmospheric Metal Deposition" was held at the University of Berne, Switzerland, to evaluate the authenticity of peat bog records of atmospheric metal deposition, and to compare them with those obtained from other archives such as ice cores and lake sediments. The outcome of the workshop was summarised and published in a special issue of Water Air and Soil Pollution (Shotyk *et al.,* 1997). Most of the presentations in the workshop demonstrated the success of using peat bogs as archives of atmospheric metal deposition, especially for Pb. However, a number of questions about using peat bogs as archives of atmospheric metal deposition still remain to be resolved.

For example, it was recommended in the workshop that detailed analyses of the deeper, older sections of bogs would provide a complete and long-term high-resolution record of atmospheric metal deposition. There are large variations in Pb concentrations owing to natural processes such as volcanic emissions and enhanced fluxes of soil dust. Studies of these sections of bogs were suggested so as to provide new insights into the effect of changing climate on global metal cycling.

It was also mentioned in the workshop that ^{137}Cs and other radionuclides could be useful tracers for quantifying diffusion rates and for studying other transport processes in bogs, because, while ^{210}Pb is effectively retained in the peat column, ^{137}Cs is not. Though ^{210}Pb has been verified as a dating tool for peat cores, other independent dating techniques should also be sought for dating peat, according to the workshop. This is because the age of peat falls between the useful range of ^{210}Pb and ^{14}C.

In addition, attention was drawn to the question of plant uptake, which has been successfully avoided by many researchers who concentrated on Pb, at the workshop. It was pointed out that the effect of plant uptake on metal concentration profiles, especially with respect to Cu, Zn and other nutrient elements, should not be overlooked.

Questions as to how the deposited metals are distributed with respect to particle size, and how the particle size distribution of metals compares when they arise from natural versus anthropogenic sources, were discussed. The mechanisms of metal retention and whether or not these vary depending on the source of the metal and the size of the particle need to be considered. In addition, whether or not the anthropogenic acidification of bogs and hydrological changes induced by global warming could affect the rates of metal movement was also raised at the workshop.

In addition to further work with "anthropogenic" metals such as Pb and Hg, much basic work is needed on the "lithogenic" metals such as Hf, Sc, Ti, Y, Zr to see which function reliably as conservative, index metals against which anthropogenic enrichments can be calculated. The difference between the "background" metal concentrations in peat cores (i.e. the chemical composition of pre-anthropogenic aerosols) versus crustal abundance was also discussed. It was predicted that, in the future, studies of these differences may provide new insight into the natural enrichment of metals in soil-derived aerosols, relative to their sources.

Finally, the question of appropriate methods for sampling and analysis was raised many times during the workshop. With a wide variety of sample preparation and analysis methods, the lack of certified reference materials and the lack of uniformity in the different procedures of sample preparation used did not allow the results from different studies to be compared world-wide nor the procedures to be validated. Very recently, however, Givelet *et al.* (2004) have proposed a protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses. The results obtained are defined by the determination of extractable elements using a given method. Coal and Plant Certified

Reference Materials have been used to determine accuracy in this kind of analysis (Shotyk *et al.,* 1998, 2000). However, in view of differences from peat bog matrices, it is difficult to obtain satisfactory estimates of accuracy by using such reference materials. Some researchers have tried to develop a reference material for this kind of analysis (Barbante *et al.,* 2000), but the fen peat used had a different matrix from that of ombrotrophic peat. So certified reference materials are needed for use as quality assurance in these types of analysis. To date, no ombrotrophic peat bog reference materials with heavy metals at the trace level have been prepared with satisfactory homogeneity to permit certification and use for quality assurance purposes in the study of atmospheric metal deposition. Yet without such a reference standard as a quality control, it is difficult to demonstrate improvements in analytical methods for trace and ultra-trace elements, to make accurate assessments of atmospheric metal deposition and to carry out fundamental research on the geochemical evaluation of peat profiles.

2.4 The effects of sample preparation on the determination of elemental concentrations in peat

Usually the concentrations of heavy metals in peat cores are very low, resulting in significant difficulties in the development of reliable methods for determination of atmospheric metal deposition using peat bogs as archives. Any problems in the use of atomic absorption spectrometry and ICP-MS for trace heavy metal analysis in peat, however, are mainly associated with sample preparation. A variety of sample digestion schemes have been used without standardised methods. For this reason, comparative studies of digestion methods are required for the development of a peat bog certified reference material that eventually is characterised for all suitable dissolution methods.

Since peat has more mineral materials than plants and is less resistant to decomposition in strong acid than is coal (Shotyk, 1997), sample dissolution is mainly dependent on two approaches. They are total and acid-extractable digestion methods. Both approaches have a number of versions differing in the reagents used, the sequence and configuration of their use, and the process parameters. Further

differences can be found in quantitative parameters such as the aliquot of sample, the concentration and amounts of reagents, and the final volume of solution. Total digestion of most geological samples is attained by the use of hydrofluoric acid or fusion with lithium borate. However, the most appropriate digestion method for the study of peat bog material has still not been agreed. As a result, the ensuing variety of existing methods for sample preparation, modified from the dissolution of soil samples, leads to difficulties in interpreting the analytical results. Most peat digestion methods involve digesting either on a hot plate or via the assistance of microwave system with one or more of HNO_3, $HClO_4$, H_2SO_4, HCl, and H_2O_2 (Farmer *et al.*, 1997; Norton *et al.*, 1997; Brannvall *et al.*, 1997; Shotyk *et al.*, 1997; Gilberton *et al.*, 1997; Kuster *et al.*, 1997; Steinnes., 1997). A wide range of sample digestion methods used in geological samples (soil, lake sediment, and peat) are summarised in Table 2.2.

Table 2.2 Summary of sample digestion methods for geological samples.

Reagents & Procedures	Samples	References	Comments
HF + $HClO_4$, H_3BO_3, HCl digestion (conventional heating),	soils	Kowalewska *et al.*, 1998	Provides high accuracy and satisfactory precision with a few percent RSD.
HF + $HClO_4$, H_3BO_3 digestion followed by fusion with $LiBO_2$ (conventional heating)	soils	Kowalewska *et al.*, 1998	Addition of $LiBO_2$ is not necessary, and the result turns out to be less effective.
HF + HCl + HNO_3, H_3BO_3 digestion (microwave heating)	soils	Kowalewska *et al.*, 1998	The digestion takes place in a closed vessel of microwave system yielding a complete dissolution.
Leaching procedure by using HNO_3 + $HClO_4$, HCl,	soils	Kowalewska *et al.*, 1998	Gives results lower than the certified value and additionally shows rather poor precision.
Ashing, followed by dissolution with 6 M HCl in a hot sand bath for 2 h	Organic residues	Moral *et al.*, 1998	Ashing method may be adequate in most of the cases and could be used to estimate the concentration of metals in organic residues.
HNO_3 and H_2O_2 (microwave digestion)	Organic residues	Moral *et al.*, 1998	Microwave digestion seems to be a more reliable process to be applied for organic residues, due to the closeness of results with the certified value.

2.4.1 The utilisation of standardised methods for geological sample preparation

In addition to Table 2.2, another method is the standard digestion method for total elemental analysis of soil material by the Soil Survey Laboratory (USDA Natural Resources Conservation Service) (Wilson *et al.,* 1997). In this method, the suspended clay was digested with hydrofluoric acid. The accuracy and efficiency of elemental recovery were compared with a few other methods (digestion of dried sample with HF, digestion of dried sample with HF and *aqua regia*, microwave digestion of samples with HF and *aqua regia* in Teflon bombs, and sample digestion by Li metaborate fusion). Their results indicated that a combination of HF and *aqua regia* yielded the best statistical agreement of elemental concentrations with the certified values. The result led to a change in the standard SSC digestion method to digestion of the dried sample with hydrofluoric acid and *aqua regia*, and resulted in a new standard SSC digestion method for total elemental analysis at the USDA Soil Survey Laboratory, Lincoln, Nebraska.

The USEPA (U.S. Environmental Protection Agency) Method of Digestion has also been adopted in the preparation of geological samples. A comparison of USEPA Methods 3050 and 3051, namely hot plate and microwave digestion, was carried out by Wei *et al.* (1997). After that, USEPA digestion methods [3050 (hotplate, HNO_3 – HCl, acid-extractable digestion method), 3051 (microwave, HNO_3, acid-extractable digestion method), 3051a (microwave, HNO_3 – HCl, acid-extractable digestion method), and 3052 (microwave, HNO_3 – HCl – HF, total digestion method)] were compared by Chen and Ma (1998). Acid-extractable digestion methods, a common approach for sample preparation in trace metals analysis, have been used in many environmental studies, including monitoring the mobility of heavy metals and estimating total elemental concentrations for site assessment purposes. Chen and Ma (1998) found that, among these four digestion methods, the microwave-assisted USEPA Method 3052 achieved satisfactory recoveries for all trace elements. This finding was in agreement with the studies by other researchers, who concluded that the utilisation of HNO_3 – HCl – HF, with the assistance of microwave digestion, provided satisfactory recoveries and precision for all trace elements.

Falciani *et al.* (2000) reported that USEPA method 3051, using concentrated nitric acid, does not provide a total digestion for many samples. Moreover, after microwave digestion, not only has the vessel content to be filtered or centrifuged to remove any remaining undissolved particles, but also some elements of interest bound in silicate structures will not have been dissolved. He also revealed that, although dissolution procedures incorporating H_2SO_4, in order to generate more vigorous acid digestion conditions, can result in very clear solutions, they can cause low recovery of some elements, such as Pb and Ba. He also found that the utilisation of H_2O_2 for digestion did not result in more effective dissolution compared with the acid mixture HNO_3-HF. As a result, the acid mixture HNO_3-HF was adopted as the method of digestion in their experiments.

Meanwhile, Quevauviller *et al.* (1998) used single and sequential extraction methods in the certification of soil and sediment reference materials. The single and sequential extraction methods had been developed and used for evaluating the metal fractions available to plants and the environmentally accessible trace metals by the early 1980s (López-Sánchez *et al.,* 1998). The sewage sludge amended soil certified reference material, CRM 483, was certified in 1997 for its EDTA and acetic acid extractable contents of Cd, Cr, Cu, Ni, Pb and Zn. According to this method, it seems likely that a standardised sequential extraction method may be suitable for extraction of trace metals in certain environmental samples. However, recent revision has recommended that *aqua regia* extraction (following the ISO 11466 Standard) be employed in the last step of extraction for CRM483 (Rauret *et al.,* 2000). The digestion method according to ISO Standard 11466 has been proposed for the determination of extractable metals in soils and similar materials containing less than about 20% m/m organic carbon according to ISO 10694.

Krachler *et al.* (2002) proposed a simple, robust and reliable analytical procedure for the determination of elements (Ca, V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Ag, Cd, Ba, Tl, Th and U) in peat and plant materials by inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS). The digestion method was carried out in a microwave heated high-pressure autoclave using 3 ml HNO_3 and 0.1 ml HBF_4, as they found that in almost all cases HNO_3 could not fully digest the analytes of interest from the peat

or plant matrix, probably because of the silicates present. After adding small amounts (0.05 – 0.1 ml) of either HF or HBF_4 to the digestion mixture, concentrations quantified by ICP-QMS generally increased significantly, in the case of Rb by up to 80%. Further increasing the volumes of HF or HBF_4 resulted in a decrease of recoveries for almost all elements, some of which amounted to approximately 60%. The analytical procedures generated concentrations that were in good agreement with results from an inter-laboratory trial or from instrumental neutron activation data.

2.5 General principles and requirements for preparation of certified reference materials

In the preparation of certified reference materials, there are numerous considerations. This section contains a discussion of terms and methods involved in the preparation of certified reference materials; *Quality assurance, Reference material terminology, Preparation of reference materials and Selection of starting material, Homogenisation and testing, Storage and stability, Certification of reference materials, and Contents of certificates of certified reference materials.*

2.5.1 Quality assurance

"*Quality assurance*" involves two concepts; *quality control* and *quality assessment. Quality control* is the mechanism established to control errors, while *quality assessment* is the mechanism used to verify that the measurement system is operating with acceptable limits. Quality control serves to detect unexpected deviations, and quality assessment is needed to ascertain that the uncertainty of results reported by a laboratory does not exceed its limits (Parr and Stoeppler, 1994).

2.5.2 Reference material terminology

There is a lack of uniformity in the use of technical terms in this field (Parr and Stoeppler, 1994). Terms such as control material, reference material, research material, standard reference material and certified reference material can be found in the literature published by organisations that produce such materials. Producers would cause less confusion if they used some of the vocabulary recently adopted by four international standards organisations, namely BIPM (International Bureau of Weights and Measures), IEC (International Electrochemical Commission), ISO (International

Organisation for Standardisation) and OIM (International Organisation of Legal Metrology). According to these organisations, a reference material is a material or substance which is sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. A certified reference material is a reference material for which values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation, which is issued by a certifying body.

The ISO Guide 30 (ISO Guide 30–Second edition (E), 1992,) from which these definitions are drawn, proceeds further to define the following quantities:

Certified value, for the CRM, is the value that appears in the certificate accompanying the material.

Uncertified value, value of quantity, is included in the certificate of a CRM or otherwise supplied, provided for information only but not certified by the producer or the certifying body.

Consensus value (of a given quantity), for a reference material, is the value of the quantity obtained by inter-laboratory testing, or by agreement between appropriate bodies or experts. (Note: A consensus value could, through appropriate action by a certifying body, become a certified value.)

Uncertainty of certain value is an estimate attached to a certified value of a quantity which characterises the range of values within which the "true value" is asserted to lie with a stated level of confidence.

Precision is the closeness of agreement between independent test results obtained under prescribed conditions (ISO 5725-1986(E), 1986).

Accuracy is the closeness of agreement between a test result and the accepted reference value (ISO 5725-1986(E), 1986).

Accepted reference value is a value that serves as an agreed-upon reference for comparison and which is derived as:

a) a theoretical or established value, based on scientific principles;
b) an assigned value, based on experimental work of some national or international organisation;
c) a consensus value, based on collaborative experimental work under the auspices of an engineering group. (ISO 5725-1986(E), 1986).

Traceability is the property of the result of a measurement or the value of a standard whereby it can be related, with a stated uncertainty, to stated references, usually national or international standards, through an unbroken chain of comparisons.

2.5.3 Certification of reference materials

Although certification is the desirable end goal of the procedure used to establish the composition of a reference material, producers are also concerned with lesser degrees of certainty such as those represented by consensus values, best estimates or even "information values" (Parr and Stoeppler, 1994).

2.5.3.1 Certification procedures

According to ISO Guide 35 (ISO Guide 35-1985(E), 1985), there are three different measurement approaches, or combinations of these three, used by certifying bodies;

a) Measurement by a single definite method in a single laboratory.
   The method is usually performed by two or more analysts working independently. Frequently, an accurately characterised back-up method is employed to provide additional assurance that the data are correct.
b) Measurement by two or more independent reference methods in one laboratory.
   The methods must have small estimated inaccuracies relative to the end-use certification requirement.
c) Measurement by a network of qualified laboratories using one or more methods of demonstrated accuracies.

For (a), the Comité Consultatif pour la Quantité de Matière (CCQM) has defined a definite method or primary method of measurement as a method which is completely described and understood, having the highest metrological qualities and for which the results can be given with a complete uncertainty statement. Recently, ID-ICPMS has been recognised by the CCQM as a primary method of measurement (Prohaska *et al.*, 2000). However, the second (b) and third (c) methods are more widely used than the first one. Method (b) is the most commonly used by National Institute of Science and Technology (NIST), and (c) is the most commonly used, e.g. by Community Bureau

of Reference (BCR) and International Atomic Energy Agency (IAEA) (Parr and Stoeppler, 1994).

Each of these procedures has its own advantages and disadvantages. But each, if properly applied, is capable of leading to reliable certification. The methods used by a network of qualified laboratories should involve statistical tests to eliminate outliers. In addition, there are various acceptance criteria to be used. The most important criterion is that data should be available from at least two different analytical methods for the calculation of the consensus value, and that there should be no significant differences between the groups of accepted results obtained by different analytical methods.

2.5.3.2 Contents of certificates

According to ISO Guide 31 (ISO Guide 31-1981(E), 1981), there are various kinds of information which should be included in certificates of reference materials. They include; (1) name and address of the certifying organisation; (2) title of the document; (3) status of the certificate; (4) name of material; (5) sample number and/or batch number; (6) date of certification; (7) availability of other forms/sizes of the reference materials; (8) source of the reference material; (9) supplier of the reference material; (10) preparer of the reference material; (11) description of the reference material; (12) statement of intended use; (13) stability, transportation and storage instructions; (14) special instructions of correct use; (15) method of preparation; (16) statement of homogeneity; (17) certified property values and their uncertainty; (18) secondary property values given for information but not certified; (19) special values obtained by individual laboratories or methods; (20) meaning of the statistical uncertainty; (21) measurement techniques used for certification; (22) names of analysts, investigators, and participating laboratories; (23) legal notice; (24) reference (including companion report if any); (25) signatures or names of certifying officers.

One of the most important requirements is to reach agreement on how to express the uncertainties in the certified values and to make the meanings of these quantities more comprehensible to the user. According to ISO Guide 35 (ISO Guide 35-1985(E),

1985), there are two different kinds of confidence interval. One is the confidence interval of the mean (usually expressed as the 95% confidence level, taking account of the degrees of freedom implied by the number of measurements). The other is the statistical tolerance interval, which may be applied to materials in which unit-to-unit variation (inhomogeneity) is not negligible compared to the measurement uncertainty. The tolerance interval is usually constructed so that it will cover 95% of the population with a probability of 99%. Both these ways of expressing certified values and their uncertainties are based on the assumption of normal statistics.

2.5.4 Preparation of reference materials

Preparation should be carried out in such a way as to ensure minimisation of heterogeneity and instability, in conjunction with improvement of the mechanical properties of the material. Care should be taken to avoid contamination which could introduce inhomogeneities to a homogeneous material. The material should be then transformed into an optimal physical and chemical form. To keep the material in this form, it should be stored in a tight and inert container. To minimise degradation the water content of the candidate material should be reduced to a very low level. Water activity is defined as the relative humidity with which a material is in equilibrium. Microbiological degradation cannot occur at water activities below 60%. Degradation due to enzymatic activity and non-enzymatic browning are very low at water activities below 30%. The autoxidation rate is lowest for water activities between 15 and 40%. This means that degradation increases if the material is too dry. Apart from autoxidation, condensation reactions are possible at too low water activities. Taking these into account, it is recommended that water activities between 0.15 and 0.30 appear to ensure the minimum possible degradation rate. Care should be taken to store the material at the correct temperature from an early point in the production process in order to minimise the probability of the degradation processes (Linsinger *et al.*, 2001a).

2.5.4.1 Selection of starting material

Apart from avoiding contamination of starting material, the ideal goal of producing an appropriate reference material is that it not only has the same matrix as that of the

samples to be analysed but also matches them with respect to the levels of the trace elements of interest. One important feature of the reference material is that speciation (i.e. the valency and chemical binding of trace elements) should be the same as in the sample matrix. In other words, reference materials should be made of natural products with a similar matrix to that of the samples to be analysed (Parr and Stoeppler, 1994).

A further important requirement in selecting the starting material is that after all the processing has been done to produce the end product, a large amount of final product reference material should remain to permit meaningful use of this material over a period of several years. Most producers do not provide details of how much is available for distribution. Some organisations have adopted the criterion that, for a trace element reference material, at least 50 kg of the final end product should be produced. And some 15 kg have been produced in other organisations (Parr and Stoeppler, 1994).

In the preparation of Sewage sludge-amended soil (CRM 483), Calcareous soil (CRM 600) and Terra rossa soil (CRM 484), as conducted by Quevauviller *et al.* (1998), 300 kg of starting material was collected by multiple sampling to a depth of 10 cm and bulked into polyethylene bags for transport to the laboratory. The whole soil was air-dried at 30°C for 1-3 weeks on paper-lined aluminium trays, and the dried material was then gently rolled with a wooden roller to break up large aggregates, sieved through a 2 mm round-hole sieve and stored in tightly sealed polyethylene bags for study of homogenisation.

2.5.4.2 Homogenisation and homogeneity testing

One of the critical steps in preparing a reference material is homogenisation. Generally, this is accomplished by using commercially available ball or disc mills, a mixing drum, or the coning and quartering method. The process can also be assisted by passing the material through a sieve. Nylon sieves with a mesh size of 125 μm are generally used for this purpose.

For practical reasons, homogeneity cannot usually be tested for every element of interest. At the IAEA, (Parr and Stoeppler, 1994), homogeneity is checked by analysis of one or more major elements (e.g. sodium) and one or more trace elements (e.g. zinc) of several sub-samples from various bottles chosen at random. For homogeneity tests of a number of trace elements, the solid sampling AAS technique can also be used with an appropriate number of sub-samples weighing around 1 mg, or even less, from various bottles. On the basis of such measurements, the homogeneity is usually better than 2% relative standard deviation (RSD) for samples of ≥ 100 mg dry weight.

In the preparation of Sewage sludge-amended soil (CRM 483), as carried by Quevauviller *et al.* (1998), the soil sample was thoroughly mixed and homogenised by rolling on a clean polyethylene sheet for three days with occasional mixing by hand. The whole sample was then gently poured onto a clean polyethylene sheet, mixed, and coned and quartered by hand. The initial sample, nominally 150 kg of air-dried (< 2 mm) soil, was split by coning and quartering, bulking opposite quarters to form the half samples, and setting one of the half samples aside. The remaining half sample was again coned and quartered. The coning and quartering procedure continued until the half-sample weight was approximately two kg. From opposite quarters of this half-sample, 20 sub-samples were taken alternately by nylon spatula into pre-cleaned brown glass bottles (capped by polyethylene screws-cap). Each of the bottles contained approximately 70 g of sample. A total of 1,280 bottles was obtained and 128 bottles (two from each final half-sample) were set aside for homogeneity and stability testing.

For Calcareous soil (CRM 600) and Terra rossa soil (CRM 484) (Quevauviller *et al.*, 1998), the air-dried (< 2 mm) soil sample was mixed in a mixing drum filled with dry argon and placed on a roll-bed for over 4 weeks. Ten sub-samples were taken from the centre of the drum for a preliminary check of the homogeneity. After the material had been thoroughly homogenised, the sample was further homogenised by mixing in the drum for three days. To prevent segregation of the fine particles, 10 samples were taken from the centre of the drum immediately upon stopping the rotation of the mixing drum. These samples were placed into 10 pre-cleaned brown glass bottles, each containing a minimum of 70 g of soil, and stoppered. The drum was again

rotated for a further 2 minutes and a further 10 samples were sub-sampled in the same way into bottles. The sub-sampling and bottling operation was continued until 1,000 bottles of the soil were obtained. The residual soil material, amounting to about 10% of the whole, was discarded because earlier experience suggested that this might be less homogeneous. One hundred bottles, selected sequentially over the whole bottling procedure, were tested for homogeneity and stability testing (Quevauviller *et al.*, 1998). The homogeneity study was carried out by analysing six elements (Cd, Cr, Cu, Ni, Pb and Zn) in 10 sub-samples taken from one bottle of each candidate CRM (within-bottle homogeneity test). The CVs and the total uncertainty U_{cv} for the extractable trace element contents between (S_b) and within (S_w) bottles were calculated. An *F*-test was used to test for significant difference between the within-bottle and between-bottle test results.

In homogeneity testing, there are two types of homogeneity testing that must be considered. First, there is the within-bottle homogeneity, which indicates the minimum sample intake, for which the established uncertainty is still valid. Secondly, there is the between-bottle homogeneity, which deals with the bottle-to bottle variation. The common element in both types of experiments is that a separation between the effect (heterogeneity) and the variability of measurement should be established. In order to do so, it is most advantageous to carry out a within-bottle homogeneity study with a very small amount of sample, so that the between-bottles effect can be calculated. After completion of this test, the minimum sample intake can then be calculated. For a between-bottle homogeneity testing, it is recommended taking the optimal sample intake for the chosen method to minimise analytical variation. The between-bottle variation should be quantified by the analysis of variance (ANOVA).

2.5.4.3 Storage and stability

The stability of a reference material is of great importance since the same material may be used over a period of many years. At issue is not only the question of whether it continues to be favourable to handle, but also, due to evaporation or chemical reactions, whether the concentrations and chemical binding of some of the elements of interest may change. This is obviously of greatest concern for elements that can exist in a volatile form, such as mercury and arsenic, which could thereby be lost.

Two types of stability testing should be carried out, including one study at elevated temperature to elucidate whether any degradation can be expected during transportation. This study is conducted in a short period of time, normally not longer than four weeks. Based on results of this study, transport conditions must be chosen to ensure that the contribution of short-term stability is negligible. In this case, uncertainty from short-term stability can be eliminated. A second study must be conducted at storage temperature to obtain information about the stability during storage. Simulation of long-term storage by harsh conditions is usually not appropriate, as the degradation mechanism might change. Estimating stability data by extrapolating data from higher temperatures via the Arrhenius-equation is not recommended, as usually the processes underlying stability problems are too complex to be modelled. Stability should be evaluated at storage temperature. Usually, a stability study consists of a series of measurements performed at different times. If the temporal trend is significant, uncertainty of long-term stability is calculated by regression analysis. However, in many cases these evaluations do not yield quantitative results, especially if the candidate material is prepared in a way to ensure optimal stability (Linsinger *et al.,* 2001a). According to ISO (ISO Guide 31-1981 (E), 1981), the period of validity of the reference material should be stated by the issuing organisation. However, in practice, this is usually not done for the simple reason that the producer has no reliable means to determine the life-span of the product.

For Sewage sludge-amended soil (CRM 483), Calcareous soil (CRM 600) and Terra rossa soil (CRM 484) (Quevauviller *et al.*, 1998), the stability of candidate reference materials was tested by keeping the candidate reference materials at –20, +20 and +40°C for a period of 12 months. After 1, 3, 6 and 12 months, the extractable contents of various elements (Cd, Cr, Cu, Ni, Pb and Zn) in the candidate reference materials were determined (in five replicates). The procedures used were the same as in the homogeneity study. Instability would be detected by comparing the contents of different analyses in samples stored at different temperatures with those stored at a low temperature at the various occasions of analysis.

The samples stored at –20°C were used as reference for the samples stored at +20°C and +40°C, respectively. The ratios (R_T) of the mean values ($\overline{X}_T$) of 5 measurements made at +20 and +40°C and the mean value ($\overline{X}_{-20°C}$) from 5 determinations were calculated as;

$$R_T = \overline{X}_T / \overline{X}_{-20°C}$$

In the case of ideal stability, the ratios R_T should be 1. In practice, however, there are some random variations due to the error on the measurement. In almost all the cases, the value 1 lies between $R_T - U_T$ and $R_T + U_T$. The uncertainty U_T was obtained from the coefficient of variation (CV) of 5 measurements obtained at each temperature (Quevauviller *et al.*, 1998);

$$U_T = (CV_T^2 + CV_{-20°C}^2)^{1/2} \cdot R_T.$$

2.5.4.4 Estimation of uncertainty of measurement in a reference material certified by inter-laboratory comparison

According to the Guide to the Expression of the Uncertainty in Measurement (GUM), the uncertainty of a value assigned to a reference material certified by inter-laboratory comparison consists of four building blocks: (Linsinger *et al.*, 2000; Pauwels *et al.*, 2000)

1. Uncertainties from characterisation (u_{char})
2. Uncertainty from homogeneity (u_{bb})
3. Uncertainty from long-term stability under storage conditions (u_{lts})
4. Uncertainty from short-term stability during transportation (u_{sts})

The overall relative uncertainty can be modelled as the sum of these uncertainties:

$$U_{CRM} = k\sqrt{u_{char}^2 + u_{bb}^2 + u_{lts}^2 + u_{sts}^2} \quad ; \text{where}$$

U_{CRM} = expanded uncertainty of the certified reference material

k = coverage factor

u_{char} = uncertainty of the certified property of the batch

u_{bb} = between-bottle inhomogeneity

u_{lts} = uncertainty of long-term stability (storage)

u_{sts} = uncertainty of short-term stability (transportation)

2.5.4.4.1 Estimation of U_{char}

U_{char} can be split into exclusively laboratory independent uncertainties (e.g. experimental standard deviation), uncertainties common to all laboratories (e.g. use of the same extinction coefficient with a stated uncertainty), uncertainties common to groups of laboratories, and a residual uncertainty (related to the differences between laboratory averages) (Pauwels *et al.,* 1998a). U_{char} was therefore modelled as shown in Equation (1) below:

$$U_{char} = \sqrt{[u(I)]^2 + [u(II)]^2 + [u(III)]^2 + [u(R)]^2} \qquad (1)$$

where

$u(I)$ = exclusively laboratory-dependent uncertainty

$u(II)$ = uncertainty common to all laboratories

$u(III)$ = uncertainties common to groups of laboratories

$u(R)$ = residual uncertainty

However, as any difference in laboratory average is either caused by bias or random variation, the residual uncertainty term can be dropped to avoid the inclusion of this effect twice (Linsinger *et al.*, 2000). So equation (1) can be reduced to equation (2):

$$U_{char} = \sqrt{[u(I)]^2 + [u(II)]^2 + [u(III)]^2} \qquad (2)$$

Each term can be calculated as:

1. Exclusively laboratory dependent uncertainty, $u(I)$,

$$u(I) = \frac{\sqrt{\sum_{i=1}^{l} [u_{c,i}]^2}}{l}$$

where

l = total number of laboratories

$u_{c,i}$ = combined uncertainty of laboratory I

However, as mentioned by Linsinger *et al.* (2000), frequently only raw data (without any uncertainty statement) are submitted from the participants. However, laboratory uncertainty can be assumed to consist of two parts: statistical part and systematic part. The systematic part is systematic only for this measurement series, but is statistical

when investigated over several series. Its variance $Var(syst_i)$ is part of the overall uncertainty of laboratory i. Thus, the uncertainty of laboratory i can be written as (Linsinger *et al.*, 2000):

$$u_{c,i} = \sqrt{\frac{s_i^2}{n_i} + Var(syst_i)^2}$$

where

s_i = standard deviation of the results of laboratory i

n_i = number of replicates of laboratory i

$Var(syst_i)$ = variation of the systematic deviation of laboratory I

The mean systematic deviation for each laboratory is zero with an unknown variation $Var(syst_i)$. As an approximation, all laboratories will perform equally well, which means that they will have the same variation in this systematic term. In this case, the standard deviation between laboratories from ANOVA statistical testing can be used as an estimation for the variation in this systematic term. Therefore $u(I)$ can be written as (Linsinger *et al.*, 2000):

$$u(I) = \frac{s}{\sqrt{l}}$$

where

s = standard deviation of laboratory means

l = number of laboratories

2. Uncertainty common to all laboratories, $u(II)$, (Pauwels *et al.*, 1998a; Linsinger *et al.*, 2000).

$$u(II) = \sqrt{\sum_{i=1}^{n} [u_i(II)]^2}$$

where

i = category II uncertainty identification number, varying from 1 to n

3. Uncertainty common to groups of laboratories, $u(III)$, (Pauwels *et al.*, 1998a; Linsinger *et al.*, 2000).

$$u(III) = \sqrt{\frac{\sum_{q=1}^{g} h_q [u(q)]^2}{gl}}$$

where

$$u(q) = \sqrt{\sum_{i=1}^{n}[u_i(q)]^2}$$

where

q = group identification number, varying from 1 to g

g = total number of groups

l = total number of laboratories

h_q = number of laboratories in group q

i = category III uncertainty identification number in group q, varying from 1 to n

2.5.4.4.2 Estimation of U_{bb}

Only variation between different units of a certified reference material must be included in the uncertainty, since within-unit variation will be defined by the minimum sample used for analysis. Generally, between-bottle variation is determined by analysis of several units of the material. If only one sub-sample per unit is taken, the experimental standard deviation consists of between-bottle variation, within-bottle variation for the sample size used and intrinsic analytical variation. For several sub-samples per unit, the influence of the within-bottle variation for the sample size used and intrinsic analytical variation is reduced by $\sqrt{n}$ as shown in the equation below (Pauwels *et al.*, 1998b; Linsinger *et al.*, 2000):

$$u_{c(bb)} = \sqrt{u_{bb}^2 + \frac{s_{method}^2}{n}}$$

where

$u_{c(bb)}$ = standard deviation of the averages for each unit of the between-bottle study

u_{bb} = between unit variation

S_{method} = combined effect of within-unit variation and analytical variation

n = number of sub-samples per unit in the between-bottle study

S_{method} can be determined independently by analysing several sub-samples of one unit. In the case that n sub-samples are taken from each of i units, u_{bb} can be estimated as the standard deviation between units as calculated from an ANOVA statistical testing (Pauwels *et al.*, 1998b; Linsinger *et al.*, 2000; Van der Veen *et al.*, 2000, 2001):

$$u_{bb} = \sqrt{\frac{MS_{among} - MS_{within}}{n}}$$

where

MS_{among} = mean square among units

MS_{within} = mean square within units

n = number of sub-samples per unit

2.5.4.4.3 Estimation of u_{lts}

u_{lts} is the uncertainty related to possible degradation of the certified reference material during storage. It can be estimated from either explicit stability studies or from experience (type B evaluation). Stability studies are always conducted by storing the candidate reference material at the higher temperature (accelerated degradation and evaluation via the Arrhenius equation). If regression data are available, the slope can be tested for significance and u_{lts} can be estimated from this data (Pauwels *et al.*, 1998c; Linsinger *et al.*, 2001b; Ellison *et al.*, 2001).

2.5.4.4.4 Estimation of u_{sts}

u_{sts} is the uncertainty about changing during transport. This is usually tested by exposing the candidate material to harsh conditions (high temperature, etc.). An approach similar to u_{lts} would primarily reflect the variability of the measurements themselves, which are also the main influence on u_{sts}. Estimation of u_{sts} via regression over the short-time stability study would therefore double count this effect. Therefore, it is proposed that a short-term stability study should be conducted. In some cases, transport conditions have been studied in a way that u_{sts} can be assumed negligible (Linsinger *et al.*, 2000). However, in the study of the production of low cost quality control reference material (Walker *et al.*, 2001), u_{sts} can be omitted.

2.6 Specific aims and objectives of this research

The primary aim of this project, therefore, was to develop an ombrotrophic peat bog certified reference material, characterised for both total and acid-extractable digestion methods. The peat bog candidate reference material developed could then be used as a quality control in the study of atmospheric metal deposition via application to the determination of vertical profiles of inorganic elements in collected peat bog cores.

To achieve the aims of the project, several practical objectives were planned.

1. Determination of suitable acid digestion methods for peat material.
2. Production of a reference material from initial collection of peat through preparation of a candidate peat reference material to investigation of its homogeneity and stability.
3. Certification of the candidate peat reference material via an international inter-laboratory comparison exercise.
4. Confirmation of certified values for some elements via the primary method of measurement, isotope dilution (ID) ICPMS.
5. Application of the certified reference material as a quality control in the determination and investigation of concentration versus depth profiles of inorganic elements in cores from Flanders Moss ombrotrophic peat bog, Scotland.

Chapter 3

Development of Methods for the Determination of Inorganic Elements in Peat

Sample preparation is one major problem encountered in the determination of metals in peat. A variety of sample digestion schemes, which provide total and acid-extractable elemental concentrations, have been used by different research groups. The total concentrations of elements can be determined by using non-destructive analytical techniques (XRF, INAA, etc.) or destructive analytical techniques employing ashing procedures, such as mixtures of mineral acids with HF for wet ashing or dissolution after dry ashing, alkaline fusion etc, followed by AAS, ICP-OES, ICP-MS etc. The acid-extractable concentrations of elements are conventionally defined by the procedures involving extraction with aqua-regia, boiling 2 M HNO_3, or cold 2 M HNO_3. Both approaches have a number of versions, differing in the reagents used, the sequence and form of their use, and the process parameters. Further differences can be found in quantitative parameters such as the size of sample, the concentration and amounts of reagents, and the final volume of solution. For these reasons, comparative study of digestion methods for preparation of peat material is required. To assess the effect of sample preparation on the analysis of peat material, four dissolution methods were considered in this project; conventional HNO_3 digestion, the adapted USEPA method 3051a (HNO_3/HCl), the adapted USEPA method 3052 (HNO_3/HF), and the standard aqua regia (HNO_3/HCl) extraction procedure according to ISO standard 11466.

Conventional HNO_3 digestion is commonly employed to achieve acid-extractable elemental concentrations in geological samples. In this study, a modified version of the USEPA method 3051 protocol (USEPA, 1994) was employed for the digestion of peat material, using microwave-assisted HNO_3 digestion. The modification, designed to enable final analyses with ICP-MS, entails ashing samples in a muffle furnace to remove organic material before digestion. The overall method consists of a representative sample of up to 0.25 g (the initial weight) being ashed at 450°C for four hours prior to digestion in 10 ml concentrated HNO_3 using microwave heating with a suitable laboratory microwave system. The sample and acid are placed in suitably inert polymeric microwave vessels. The vessel is sealed and heated in the microwave

system. After cooling, the vessel contents are filtered, evaporated to ~ 1 ml, and then diluted to volume and analysed by FAAS, GFAAS, ICP-OES, or ICP-MS.

The adapted USEPA method 3051a, a modified version of the USEPA method 3051a protocol (USEPA, 1998), was one of the others used in this study. Like the conventional HNO_3 digestion, a representative sample of 0.25 g is ashed at 450°C for four hours prior to digestion in 9 ml concentrated HNO_3 and 3 ml concentrated HCl in the microwave digestion system. HCl is added to provide more effective dissolution for some elements.

The adapted USEPA method 3052, a modified version of the microwave-assisted USEPA method 3052 protocol (USEPA, 1996), is employed to achieve total dissolution of peat material. As before, a representative sample of 0.25 g is ashed at 450°C for four hours prior to digestion in 9 ml concentrated HNO_3 and 1 ml concentrated HF in the microwave digestion system. Based on the USEPA method 3052 protocol, the amount of HF required is less than 1 ml when the sample contains less than 20 % silicate. So the amount of HF to be used in this procedure was 1 ml (for approximately 0.25 g sample) to ensure that all aluminosilicates present are completely dissolved.

The standard aqua regia extraction procedure according to ISO standard 11466 is commonly used to achieve acid-extractable elemental concentrations in the absence of a microwave digestion system. A representative sample of 1-3 g peat material is digested with aqua-regia, a mixture of concentrated HNO_3 and concentrated HCl (1: 2), under reflux condition for ~ 2 hours. The digested sample is then filtered, diluted to known volume and analysed for elemental concentration by FAAS, GFAAS, ICP-OES, or ICP-MS.

In this developmental work, a Canadian peat OGS 1878 P-6 (Barbante *et al.*, 2000) was used throughout. This material, a Carex (sedge) fen peat (~ 20% ash content), was produced by the Ontario Geological Survey in 1982. It was initially intended to develop a peat reference material, as yet uncompleted, for quality control use by laboratories in the international peat bog community. Provisional certified values

arising from an inter-laboratory comparison exercise were presented at an international conference in 2000 (Barbante *et al.*, 2000).

3.1 Study of effect of sample preparation on the analysis of reference material (Canadian peat OGS 1878 P-6) for inorganic elements

3.1.1 Comparative study of four digestion methods for the analysis of the peat material

3.1.1.1 Digestion by adapted USEPA method 3051 (conventional HNO_3 digestion)

Each portion of approximately 0.250 g Canadian peat OGS 1878 P-6 reference material was accurately weighed out. It was placed in a Teflon microwave digestion vessel with 10 ml ARISTAR HNO_3 and then digested in a CEM MARS 5 microwave digestion system. The programme used had the following features: maximum power 1200 W, 100 %, ramp 30 mins, hold 20 mins, 150 PSI, 205°C. Upon cooling, the sample was filtered through Whatman No. 542 filter paper to remove any remaining solid material. The solution was evaporated down to approximately 1 ml on a hotplate and then made up to 25 ml with 2% v/v ARISTAR HNO_3. The sample solution was finally analysed for Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn by ICP-OES.

3.1.1.2 Digestion by adapted USEPA method 3051a (HNO_3/HCl)

Each portion of approximately 0.250 g Canadian peat OGS 1878 P-6 reference material was accurately weighed out. It was placed in a Teflon microwave digestion vessel with 9 ml ARISTAR HNO_3, 3 ml of ARISTAR HCl, and then digested in a CEM MARS 5 microwave digestion system. The programme used had the following features: maximum power 1200 W, 100 %, ramp 30 mins, hold 20 mins, 150 PSI, 205°C. Upon cooling, the sample was filtered through Whatman No. 542 filter paper to remove any remaining solid material. The solution was evaporated down to approximately 1 ml on a hotplate and then made up to 25 ml with 2% v/v ARISTAR HNO_3. The sample solution was finally analysed for Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn by ICP-OES.

3.1.1.3 Digestion by adapted USEPA method 3052 (HNO_3/HF)

Each portion of approximately 0.250 g Canadian peat OGS 1878 P-6 reference material was accurately weighed out. It was placed in a Teflon microwave digestion vessel with 9 ml ARISTAR HNO_3, 1 ml of ARISTAR HF, and then digested in a CEM MARS 5 microwave digestion system. The programme used had the following features: maximum power 1200 W, 100 %, ramp 30 mins, hold 20 mins, 150 PSI, 205°C. Upon cooling, the sample was transferred to a 100 ml Teflon beaker. The solution was evaporated down to approximately 1 ml on a hotplate and then made up to 25 ml with 2% v/v ARISTAR HNO_3. The sample solution was finally analysed for Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn by ICP-OES.

3.1.1.4 Digestion by standard aqua regia (HNO_3/HCl) extraction procedure according to ISO standard 11466

Each portion of approximately 1.5 g Canadian peat OGS 1878 P-6 reference material was accurately weighed out into a 100 ml conical flask. A small amount of water (2 to 3 ml) was added to generate a slurry, and then 4.5 ml concentrated ARISTAR HNO_3 was added. After intensive foaming, 11.5 ml concentrated ARISTAR HCl was added (in several portions). The mixture was manually shaken. The flask was covered with a watch glass and left for 16 hours (overnight). A reflux condenser (a Dimroth type) of about 40 cm length was mounted on the top of the flask and the solution gently boiled under reflux for two hrs. After the samples had cooled down, the condenser was rinsed with 10 ml 2% v/v ARISTAR HNO_3, and the rinses were collected in the round-bottomed flask. The condenser was removed and the sample filtered through Whatman No. 542 filter papers to remove any undigested solid material. The filtrate was collected in a 50 ml volumetric flask. The filter and the residue were rinsed three times with 5 ml 2% v/v ARISTAR HNO_3, and the solution was then made up to 50 ml with 2% v/v ARISTAR HNO_3. The sample solution was finally analysed for Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn by ICP-OES.

3.1.1.5 ICP-OES analysis

The determination of elemental concentrations in the digested Canadian peat OGS 1878 P-6 samples was carried out by ICP-OES. A Thermo Jarrell Ash IRIS instrument was used in the analysis. Tables 3.1 and 3.2 summarise the instrumental conditions, and the analytical lines and estimated detection limits, respectively. These conditions and analytical lines were used throughout this research project. For the emission intensity/concentration calibration curves the following concentrations of all measured elements in standard solutions were used: 1.00 mg/l, 10.0 mg/l, and 100 mg/l prepared in 2% v/v HNO_3. ICP-OES calibration is linear over a wide concentration range for the determination of elemental concentration. Reagent blanks and sample blanks were included in each batch of analyses for quality control purposes.

Table 3.1 Thermo Jarrell Ash IRIS instrument operating conditions.

Power	1.40 kW
Plasma gas flow	15.0 l/min
Auxiliary gas flow	0.75 l/min
Nebuliser gas flow	0.75 l/min
Pump speed	15 rpm
Sample Delay	40 sec
Rinse time	40 sec between each sample
Replicates	3
Replicate time	30 sec
Stabilisation time	10 sec

Table 3.2 Wavelengths used for analysis and estimated detection limits (DLs) for ICP-OES.

Element	Wavelength (nm)	Estimated DLs (µg/l)
Aluminium	308.2	30
Arsenic	189.0	35
Cadmium	226.5	3
Calcium	184.0	7
Chromium	283.5	5
Cobalt	228.6	5
Copper	224.7	4
Iron	238.2	4
Lead	216.9	28
Magnesium	383.3	20
Manganese	257.6	1
Nickel	232.0	10
Phosphorus	214.9	51
Selenium	203.9	50
Sulphur	182.0	50
Titanium	338.3	5
Vanadium	311.0	5
Zinc	213:8	2

3.1.1.6 Results and discussion

3.1.1.6.1 Efficiency of digestion

The results of the different procedures used for preparation of the Canadian peat OGS 1878 P-6 are summarised in Table 3.3 and Fig. 3.1. Digestion carried out by the adapted USEPA method 3051 (conventional HNO_3 digestion), the adapted USEPA method 3051a (HNO_3/HCl), and the standard aqua regia (HNO_3/HCl) extraction procedure according to ISO standard 11466 represent acid-extractable digestion methods. The adapted USEPA method 3052 (HNO_3/HF) is a total digestion method.

The acid-extractable digestion methods did not totally dissolve the peat samples. It was therefore necessary to filter the solutions to remove undigested particles on the filter paper. The digestion carried out by the adapted USEPA method 3052 (HNO_3/HF) completely dissolved the peat material, yielding a clear solution. In addition, speed is a major advantage of microwave-assisted digestion, as it took only ~1 hr, compared with more than a day for acid digestion under reflux conditions. The other disadvantage of the aqua regia extraction method is the large amount of sample needed.

3.1.1.6.2 Accuracy and precision

The analytical results for metal concentrations in the Canadian peat OGS 1878 P-6 prepared according to the four digestion procedures are compared with certified values and summarised in Table 3.3 and Fig. 3.1. These four digestion procedures provided satisfactory precision, RSD < 5 %, and accuracy for all certified elements of interest except for Cr. There was a low recovery for Cr, as commonly found in geological analysis and usually attributed to incomplete dissolution of chromite from the sample. The total Co concentration obtained by the adapted USEPA method 3052 (HNO_3/HF) was higher than the certified value, perhaps arising from contamination with Co during the digestion process. Most significantly, however, the total Al concentration (obtained by the adapted USEPA method 3052, HNO_3/HF) was clearly higher than the acid-extractable concentrations, reflecting the requirement for HF to completely dissolve the aluminosilicates present.

3.1.1.7 Conclusions

It was decided that two digestion methods, namely the conventional HNO_3 digestion (adapted USEPA method 3051), which represents acid-extractable digestion, and the adapted USEPA method 3052 (HNO_3/HF), which yields total elemental concentrations, would be studied further in the additional experiments (3.1.2 and 3.1.3).

Table 3.3 Results of metal determination in Canadian peat OGS 1878 P-6 prepared for analysis according to the adapted USEPA method 3051 (conventional HNO_3 digestion), the adapted USEPA method 3051a (HNO_3/HCl), the adapted USEPA method 3052 (HNO_3/HF), and the standard aqua regia (HNO_3/HCl) extraction procedure according to ISO standard 11466 (confidence intervals are given at 95% level for n = 7, 8, or 9).

Element	Concentration (mg/kg)[a]				
	Certified values* (mg/kg)[a]	adapted USEPA method 3051 (HNO_3)	adapted USEPA method 3051a (HNO_3/HCl)	adapted USEPA method 3052 (HNO_3/HF)	ISO standard 11466 (aqua regia)
Al	N/A	2864 ± 104	3047 ± 62	6022 ± 349	2623 ± 141
Ca	N/A	35981 ± 603	36825 ± 413	35958 ± 836	35096 ± 902
Co	1.8 ± 0.2	2.0 ± 0.1	2.1 ± 0.1	2.7 ± 0.1	1.9 ± 0.1
Cr	8.0 ± 1.0	4.5 ± 0.3	4.3 ± 0.3	3.9 ± 0.3	2.6 ± 0.4
Cu	195 ± 16	200 ± 4	201 ± 3	190 ± 3	207 ± 8
Fe	8700 ± 600	8061 ± 139	8359 ± 118	8426 ± 133	8567 ± 250
Mg	N/A	3481 ± 64	3601 ± 64	3603 ± 91	3437 ± 126
Mn	206 ± 30	222 ± 4	230 ± 5	231 ± 4	209 ± 7
Ni	6.1 ± 0.7	7.0 ± 1.1	7.5 ± 0.9	5.9 ± 0.6	5.8 ± 1.0
Pb	78.8 ± 2.9	89.4 ± 3.9	90.8 ± 3.8	81.5 ± 3.3	92.6 ± 3.4
Zn	43 ± 3	43 ± 3	46 ± 4	46 ± 2	44 ± 2

[a] All concentration data are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat. N/A = not available.

* Barbante *et al.*, 2000

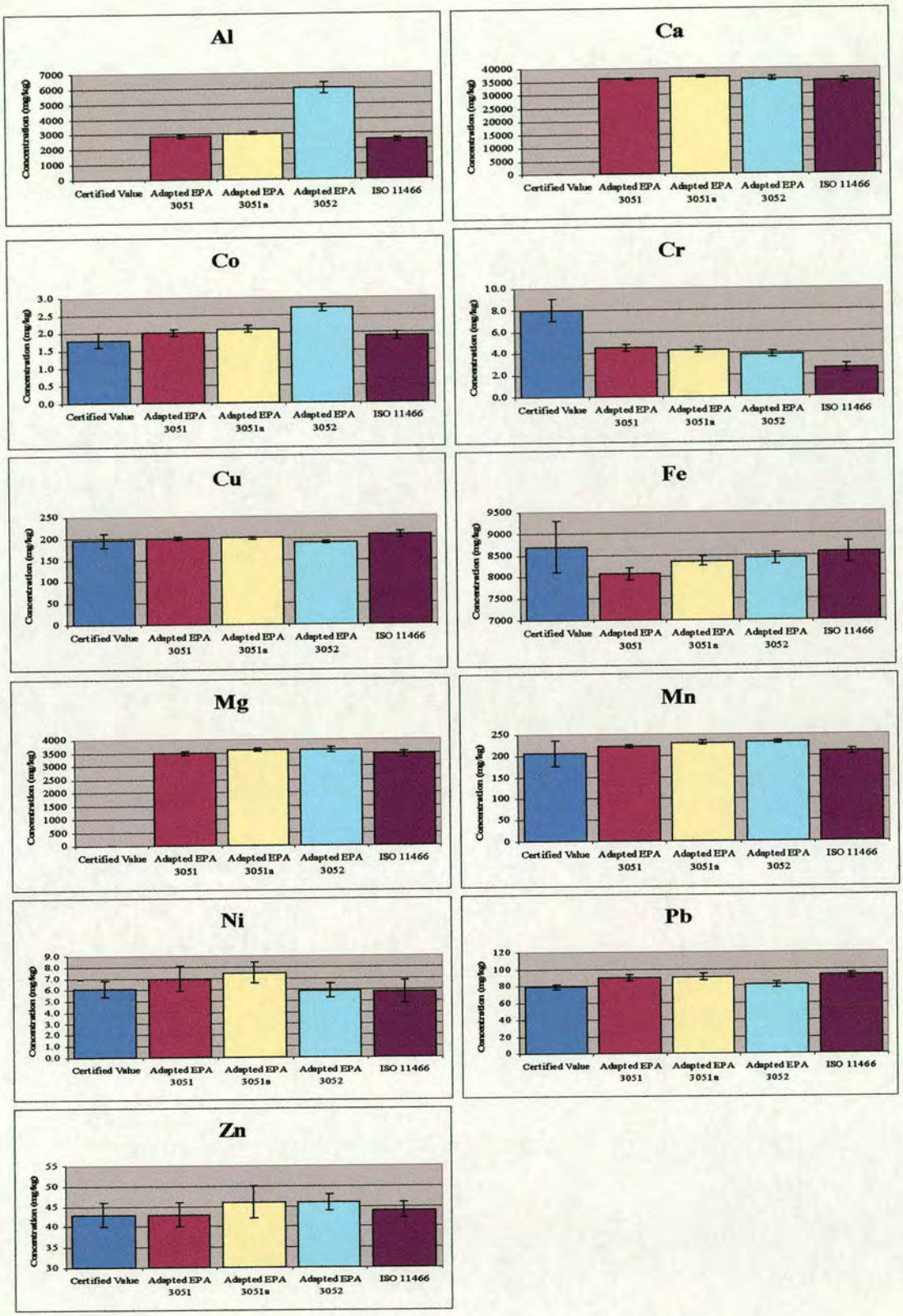


Figure 3.1 Concentrations of Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn in Canadian peat OGS 1878 P-6 reference material prepared for analysis according to four different digestion methods (the adapted USEPA method 3051 (conventional HNO_3 digestion), the adapted USEPA method 3051a (HNO_3/HCl), the adapted USEPA method 3052 (HNO_3/HF) and the standard aqua regia extraction procedure (HNO_3/HCl) according to ISO standard 11466).

3.1.2 Effects of solid sample ashing and sample digest evaporation during preparation of the peat material for analysis

This experiment investigated the effects of solid sample ashing before and sample digest evaporation after microwave-assisted digestion of the Canadian peat OGS 1878 P-6. The sample preparation method, separated into three components, was carried out by the adapted USEPA method 3051(HNO_3). For the first component, the sample was digested in the microwave unit without being ashed first. After that it was filtered, diluted to known volume, and then analysed for elemental concentration. In the second component, the sample was first ashed at 450°C prior to digestion in the microwave unit. Upon completion of digestion, it was filtered, diluted to known volume without being evaporated, then analysed for elemental concentration. For the final component, the sample was first ashed at 450°C prior to digestion in the microwave unit. The digested sample was filtered, evaporated to ~ 1 ml, diluted to known volume, and then analysed for elemental concentration.

3.1.2.1 Results and discussion

The metal concentrations determined in the Canadian peat OGS 1878 P-6 reference material, prepared for analysis according to the USEPA method 3051 (HNO_3) using the three sets of conditions, are compared with certified values in Table 3.4 and Fig 3.2. With the exception of the Zn and Ni data, for the non-ashing/non-evaporation and ashing/non-evaporation conditions, the results for the three sets of conditions are in good agreement. With the exception of all Cr data, the results are in good agreement with the certified values, where available.

3.1.2.2 Conclusions

The results demonstrated that ashing the samples before digestion by the conventional HNO_3 digestion method and evaporating them after digestion in the microwave digestion system does not adversely affect the analytical data for elemental concentrations in the peat material. Thus peat material can be ashed in the muffle furnace to remove organic matter prior to digestion with HNO_3 or HNO_3/HF in the microwave digestion system.

Table 3.4 Results of metal determination in Canadian peat OGS 1878 P-6 prepared for analysis according to the adapted USEPA method 3051 (the conventional HNO_3 digestion) with three different set of conditions: non-ashing/non-evaporation, ashing/non-evaporation, and ashing/evaporation (confidence intervals are given at 95% level for n = 7, 8, or 9).

Element	Certified values[+] (mg/kg)[a]	Concentration (mg/kg)[a]		
		Non-ashing, Non-evaporation	Ashing Non-evaporation	Ashing Evaporation
Al	N/A	2980 ± 71	2910 ± 82	2864 ± 104
Ca	N/A	36843 ± 369	38363 ± 548	35981 ± 603
Co	1.8 ± 0.2	2.0 ± 0.1	1.9 ± 0.1	2.0 ± 0.1
Cr	8.0 ± 1.0	4.2 ± 0.3	4.7 ± 0.3	4.5 ± 0.3
Cu	195 ± 16	198 ± 3	193 ± 3	200 ± 4
Fe	8700 ± 600	8212 ± 92	9185 ± 87	8061 ± 139
Mg	N/A	3588 ± 59	3448 ± 39	3481 ± 64
Mn	206 ± 30	226 ± 4	208 ± 2	222 ± 4
Ni	6.1 ± 0.7	7.2 ± 0.4	<1*	7.0 ± 1.1
Pb	78.8 ± 2.9	84.4 ± 3.8	84.3 ± 3.2	89.4 ± 3.9
Zn	43 ± 3	34 ± 2	16 ± 12	43 ± 3

[a] All concentration data are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat. N/A = not available. *Lower than limit of detection.

[+] Barbante *et al.*, 2000

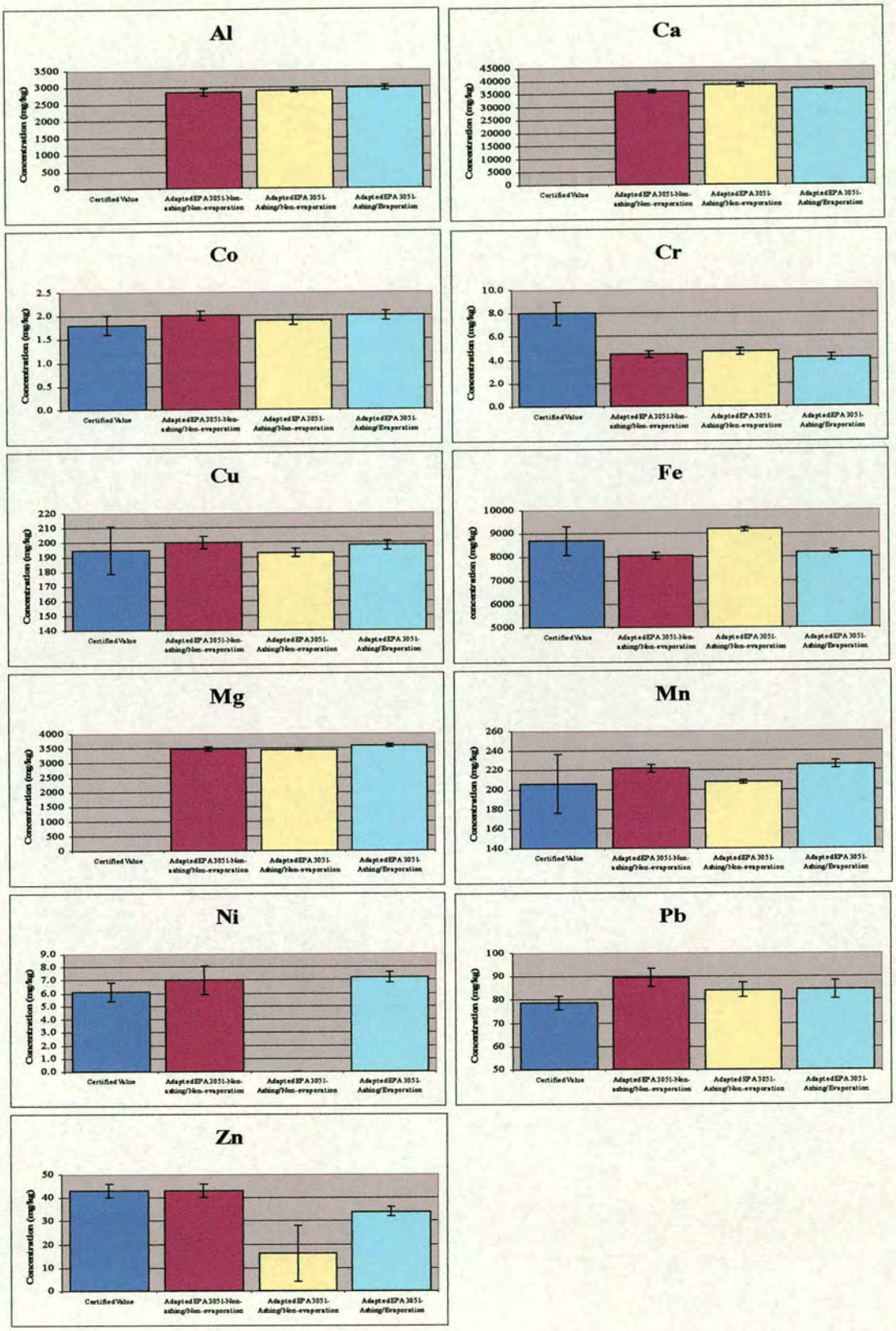


Figure 3.2 Concentrations of Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn in Canadian peat OGS 1878 P-6 reference material prepared for analysis according to the adapted USEPA method 3051 (conventional HNO_3 digestion) with three different set of conditions: non-ashing/non-evaporation, ashing/non-evaporation, and ashing/evaporation.

3.1.3 Effect of different amounts of HF on the dissolution of peat material by adapted USEPA method 3052 (HNO_3/HF)

This experiment studied the effects of different amounts of HF on the dissolution of peat material (0.25 g) by the adapted USEPA method 3052 (HNO_3/HF). The amounts of HF used were 0.5 ml, 1.0 ml, 1.5 ml, 2.0 ml, and 3.0 ml.

3.1.3.1 Results and discussion

The elemental concentrations of the Canadian peat OGS 1878 P-6 reference material, prepared for analysis according to the USEPA method 3052 using different amounts of HF, are displayed in Table 3.5 and Fig. 3.3. For most of the trace elements studied, an increasing amount of HF does not affect the results. However, increasing the amount of HF has apparently affected the results for the major elements, i.e. Al, Ca, and Mg. Above 1 ml HF, the concentration of these elements generally decrease as the amount of HF increases. This might be attributed to the formation of insoluble fluorides of these elements.

3.1.3.2 Conclusions

The amount of HF used in the adapted USEPA method 3052 (HNO_3/HF) will be 0.5 ml.

Table 3.5 Concentrations of Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn in the Canadian peat OGS 1878 P-6 reference material prepared for analysis according to the adapted USEPA method 3052 (HNO_3/HF) using different amounts of HF.

Element	Concentration (mg/kg)				
	Amount of HF (ml)				
	0.5	1.0	1.5	2.0	3.0
Al	6652	6422	3405	2453	6771
Ca	40782	41540	38596	37706	41790
Co	2.49	2.07	2.43	2.46	2.54
Cr	4.64	5.15	5.38	5.88	4.70
Cu	194	194	193	190	193
Fe	9886	9790	9880	9757	10254
Mg	3823	3814	3161	2736	3870
Mn	250	244	253	249	260
Ni	9.74	7.00	6.99	5.10	6.63
Pb	85	86	93	93	81
Zn	44.2	41.6	53.1	44.1	42.1

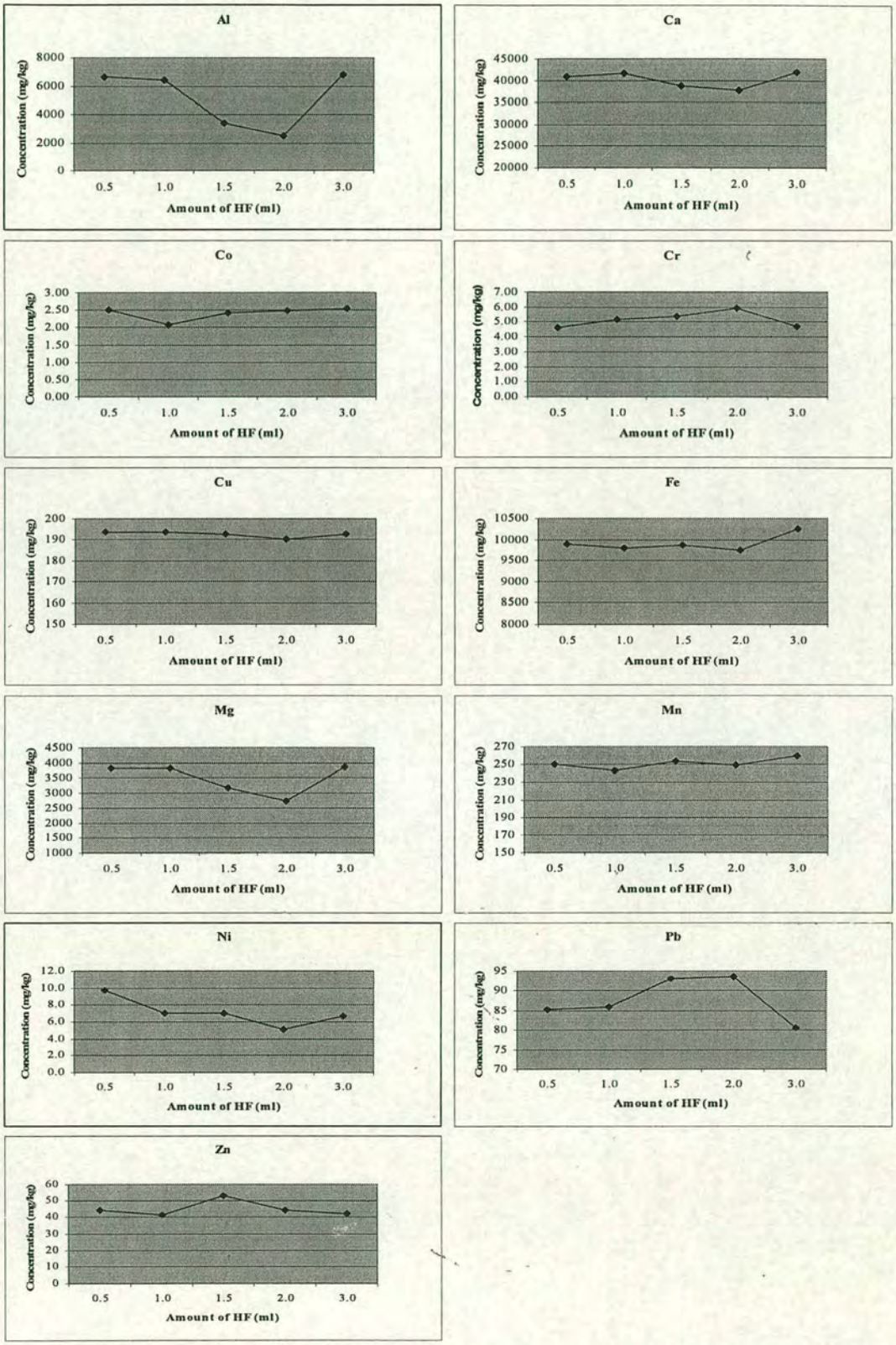


Figure 3.3 Concentrations of Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn in the Canadian peat OGS 1878 P-6 reference material prepared for analysis according to the adapted USEPA method 3052 (HNO_3/HF) using different amounts of HF.

3.1.4 Application of digestion methods for peat to other matrices

Two microwave-assisted digestion methods, the conventional HNO_3 digestion (adapted USEPA method 3051) and the adapted USEPA method 3052 (HNO_3/HF), have been chosen for further investigation as potential reference methods in the certification of ombrotrophic peat reference materials. This latest experiment was intended to confirm the analytical data for elemental concentrations in the reference material Canadian peat OGS 1878 P-6 and to investigate more elements than in the previous experiments. Moreover, this experiment applied the two digestion methods to other matrices such as leaves (Orchard leaves NBS SRM 1571) and coal (Coal NBS SRM 1635, Coal BCR 40). As previously described, the two digestion methods were modified to suit some potential final analyses with ICP-MS by first ashing the samples in a muffle furnace to remove organic material before digestion. In the last step of the digestion, HNO_3 and HF were removed from the samples by evaporating samples until almost dry and the final solution was diluted to known volume with 2% v/v HNO_3. In addition, the digestion time was shortened from 30 minutes to ~ 15 minutes. Also, the temperature of the microwave digestion system was adjusted to be lower than that of the previous experiment.

3.1.4.1 Digestion by adapted USEPA method 3051 (HNO_3)

For each of the four reference materials (Canadian peat OGS 1878 P-6, Orchard leaves NBS SRM 1571, Coal NBS SRM 1635, and Coal BCR 40), three or four portions of approximately 0.250 g were accurately weighed out. These were placed in a muffle furnace for four hours at 100°C, and for a further four hours at 450°C. After the samples had cooled down, each was placed in a Teflon microwave digestion vessel with 10 ml ARISTAR HNO_3 and then digested in a CEM MARS 5 microwave digestion system. The programme used had the following features: Temperature control, Maximum power 1200 W, 100%, Phase 1-ramp to 165°C, 3.0 mins, Phase 2-ramp to 175°C, 2.5 mins, hold at 175°C 10 mins. Upon cooling, the samples were filtered through Whatman No. 542 filter paper to remove any remaining solid material. The solutions were evaporated down to approximately 1 ml on a hotplate and then made up to 25 ml with 2% v/v ARISTAR HNO_3. The sample solutions were

finally analysed for Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, S, Se, P, Pb, Ti, V, and Zn by ICP-OES.

3.1.4.2 Digestion by adapted USEPA method 3052 (HNO_3/HF)

For each of the four reference materials (Canadian peat OGS 1878 P-6, Orchard leaves NBS SRM 1571, Coal NBS SRM 1635, and Coal BCR 40), three or four portions of approximately 0.250 g were accurately weighed out. These were placed in a muffle furnace for four hours at 100°C, and for a further four hours at 450°C. After the samples had cooled down, each was placed in a Teflon microwave digestion vessel with 9 ml ARISTAR HNO_3, and 0.5 ml ARISTAR HF, and then digested in a MARS 5 microwave digestion system. The programme used had the following features: Temperature control, Maximum power 1200 W, 100%, Phase 1-ramp to 175°C, 3.0 mins, Phase 2-ramp to 180°C, 2.5 mins, hold at 180°C 9.5 mins. Upon cooling, the samples were transferred to 100 ml Teflon beakers. The solutions were evaporated down to approximately 1 ml on a hotplate and then made up to 25 ml with 2% v/v ARISTAR HNO_3. The sample solutions were finally analysed for Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, P, Pb, S, Se, Ti, V, and Zn by ICP-OES.

3.1.4.3 ICP-OES analysis

The final analyses for elemental concentrations in digested peat samples were carried out by ICP-OES (Tables 3.1 and 3.2). The following concentrations of standard solutions for major elements were used in the calibration: 6.25 mg/l, 12.50 mg/l, 25.00 mg/l, and 50.00 mg/l prepared in 2% v/v HNO_3. For trace elements, the following concentrations of standard solutions were used: 0.25 mg/l, 0.50 mg/l, 1.00 mg/l, and 2.00 mg/l prepared in 2% v/v HNO_3.

3.1.4.4 Results and discussion

3.1.4.4.1 Efficiency of dissolution

The results of the two digestion procedures used for preparation of the Canadian peat OGS 1878 P-6, Orchard leaves NBS SRM 1571, Coal NBS SRM 1635, and Coal BCR 40 are summarised in Tables 3.6, 3.7, 3.8, and 3.9, respectively. Samples

digested by the adapted USEPA method 3051 (HNO_3) were not totally dissolved. It was therefore necessary to filter the solutions to remove undigested particles on the filter paper. Most of the samples digested by the adapted USEPA method 3052 (HNO_3/HF) yielded clear solutions and filtration was not required.

3.1.4.4.2 Accuracy and precision

The analytical results from this study indicated that these two digestion methods provided high precision (low % RSD) and accuracy for the determination of most elements of interest in the different sample matrices. It showed that these two digestion methods do not provide a reliable result for Hg, probably caused by the loss of Hg while ashing prior to and evaporating after the digestion process.

The results also confirm that these two digestion methods yield a relatively low recovery of Cr in the peat sample. Cr often gives low results in geological analysis. This is mostly attributed to the losses of Cr due to incomplete dissolution of chromite from the sample. Another possible reason for the low analytical results for Cr is the loss of Cr as volatile chromyl compounds in the ashing and evaporation steps. However, the correct results for Cr were obtained in the other matrices, except for the acid-extractable Cr concentration in Coal BCR 40.

The analytical results for Al and some major elements such as Na and Ti obtained by the total digestion method (HNO_3/HF) are closer to certified values than those obtained by the acid-extractable digestion method (HNO_3), as can be seen from the results for Orchard leaves NBS SRM 1571 and Coal NBS SRM 1635. The most accurate results for these elements are obtained by the total digestion method.

Table 3.6 Results of metal determination in Canadian peat OGS 1878 P-6 prepared for analysis according to the adapted USEPA method 3051 (HNO_3) and the adapted USEPA method 3052 (HNO_3/HF) (confidence intervals are given at 95% level for n = 3 or 4).

Element	Certified values[+] (mg/kg)[a]	adapted USEPA method 3051 (HNO_3) (mg/kg)[a]	adapted USEPA method 3052 (HNO_3/HF) (mg/kg)[a]
Al	N/A	2374 ± 261	5839 ± 1152
As	8.9 ± 0.75	<3.5*	<3.5*
Ca	N/A	39108 ± 11	37622 ± 1182
Cd	0.53 ± 0.03	<0.3*	<0.3*
Co	1.8 ± 0.2	1.8 ± 0.1	1.8 ± 0.9
Cr	8.0 ± 1.0	3.8 ± 0.6	4.9 ± 0.3
Cu	195 ± 16	201 ± 18	200 ± 7
Fe	8700 ± 600	8801 ± 798	9371 ± 356
Hg	0.089	N/A	N/A
Mg	N/A	3470 ± 301	3528 ± 437
Mn	206 ± 30	219 ± 19	235 ± 8
Na	N/A	1898 ± 147	3533 ± 167
Ni	6.1 ± 0.7	6.6 ± 0.6	8.3 ± 1.8
P	N/A	1979 ± 185	1937 ± 61
Pb	78.8 ± 2.9	84.0 ± 5.7	81.1± 5.7
S	N/A	5318 ± 440	5417 ± 512
Se	0.73 ± 0.08	N/A	N/A
Ti	N/A	96 ± 12	396 ± 46
V	9.7 ± 1.2	7.1 ± 0.9	9.0 ± 0.2
Zn	43 ± 3	43 ± 11	43 ± 2

[a] All concentration data are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat. N/A = not available. *Lower than limit of detection (Table 3.2).
[+] Barbante *et al.*, 2000

Table 3.7 Results of metal determination in Orchard Leaves NBS SRM 1571 prepared for analysis according to the adapted USEPA method 3051 (HNO_3) and the adapted USEPA method 3052 (HNO_3/HF) (values are given at 1σ for n = 2 or 3).

Element	Certified values (mg/kg)[a]	adapted USEPA method 3051 (HNO_3) (mg/kg)[a]	adapted USEPA method 3052 (HNO_3/HF) (mg/kg)[a]
Al	410	242 ± 8	394 ± 12
As	10 ± 2	9 ± 1	11 ± 1
Ca	20900 ± 300	19793 ± 1028	19298 ± 293
Cd	N/A	0.2 ± 0.1	0.3 ± 0.1
Co	N/A	0.1 ± 0.1	0.3 ± 0.1
Cr	2.6 ± 0.2	2.4 ± 0.7	2.2 ± 0.1
Cu	12 ± 1	13 ± 1	13 ± 1
Fe	300 ± 20	301 ± 18	299 ± 5
Hg	N/A	N/A	N/A
Mg	N/A	5755 ± 288	5737 ± 30
Mn	91 ± 4	94 ± 5	92 ± 1
Na	N/A	N/A	58 ± 10
Ni	N/A	2.9 ± 1.3	1.9 ± 1.0
P	N/A	1983 ± 105	1888 ± 16
Pb	45 ± 3	45 ± 2	45± 4
S	N/A	1191 ± 54	1820 ± 8
Se	N/A	N/A	N/A
Ti	N/A	14 ± 1	35 ± 2
V	N/A	0.2 ± 0.1	0.9 ± 0.2
Zn	25 ± 3	22 ± 1	27 ± 3

[a] All concentration data are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat. N/A = not available. *Lower than limit of detection (Table 3.2).

Table 3.8 Results of metal determination in Coal NBS SRM 1635 prepared for analysis according to the adapted USEPA method 3051 (HNO_3) and the adapted USEPA method 3052 (HNO_3/HF) (confidence intervals are given at 95% level for n = 3 or 4).

Element	Certified values (mg/kg)[a]	adapted USEPA method 3051 (HNO_3) (mg/kg)[a]	adapted USEPA method 3052 (HNO_3/HF) (mg/kg)[a]
Al	(3200)	2583 ± 351	2910 ± 126
As	0.42 ± 0.15	N/A	N/A
Ca	N/A	5907 ± 289	5617 ± 58
Cd	0.03 ± 0.01	<0.3*	<0.3*
Co	(0.65)	1.0 ± 0.2	1.2 ± 0.5
Cr	2.5 ± 0.3	2.1 ± 0.1	2.2 ± 0.1
Cu	3.6 ± 0.3	6.0 ± 0.2	6.1 ± 0.7
Fe	2390 ± 50	2464 ± 100	2404 ± 77
Hg	N/A	N/A	N/A
Mg	N/A	931 ± 37	909 ± 16
Mn	21.4 ± 1.5	21 ± 1	21 ± 1
Na	(2400)	2498 ± 106	2517 ± 46
Ni	1.74 ± 0.10	2.0 ± 1.1	2.7 ± 0.9
P	N/A	66 ± 6	59 ± 3
Pb	1.9 ± 0.2	2.1 ± 0.7	3.5± 2.7
S	3300 ± 300	3967 ± 714	3755 ± 313
Se	0.9 ± 0.3	N/A	N/A
Ti	(200)	172 ± 4	201 ± 6
V	5.2 ± 0.5	5.8 ± 0.6	6.7 ± 0.2
Zn	4.7 ± 0.5	N/A	(4.1)

[a] All concentration data are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat. *Lower than limit of detection (Table 3..2). N/A = not available.

Table 3.9 Results of metal determination in Coal BCR 40 prepared for analysis according to the adapted USEPA method 3051 (HNO_3) and the adapted USEPA method 3052 (HNO_3/HF) (confidence intervals are given at 95% level for n = 3 or 4).

Element	Certified values (mg/kg)[a]	adapted USEPA method 3051 (HNO_3) (mg/kg)[a]	adapted USEPA method 3052 (HNO_3/HF) (mg/kg)[a]
Al	N/A	8370 ± 1225	13498 ± 2204
As	13.2 ± 1.1	N/A	N/A
Ca	N/A	1770 ± 154	1166 ± 110
Cd	0.11 ± 0.02	N/A	N/A
Co	7.8 ± 0.6	7.2 ± 0.8	9.4 ± 1.0
Cr	31.3 ± 2.0	12 ± 1	29 ± 2
Cu	N/A	33 ± 4	25 ± 6
Fe	N/A	10016 ± 710	10413 ± 1357
Hg	0.35 ± 0.06	N/A	N/A
Mg	N/A	994 ± 90	866 ± 81
Mn	139 ± 5	132 ± 11	131 ± 20
Na	N/A	1450 ± 125	1862 ± 68
Ni	25.4 ± 1.6	22 ± 2	24 ± 1
P	N/A	59 ± 3	60 ± 4
Pb	24.2 ± 1.7	24 ± 4	25± 8
S	N/A	2214 ± 205	2314 ± 145
Se	N/A	N/A	N/A
Ti	N/A	10 ± 3	996 ± 84
V	N/A	32 ± 3	76 ± 3
Zn	30.2 ± 1.9	29 ± 6	24 ± 7

[a] All concentration data are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat. N/A = not available.

3.1.4.5 Conclusions

From this study, it can be concluded that concentrations of As, Cd, Hg, and Se arising from the application of these digestion methods to Canadian peat OGS 1878 P-6 are below the detection limit of ICP-OES. Therefore, ICP-MS will be used for some elements (e.g. As, Cd). These sample preparation methods are not suitable for Hg. The most accurate results for Al and some other major elements can be obtained only by incorporating HF into the digestion procedure. Overall, on the basis of all these experiments, two harmonised procedure digestion protocols are proposed for use in the certification of the ombrotrophic peat bog reference material.

3.2 Adapted USEPA methods for the determination of inorganic elements in peat

Two microwave-assisted digestion methods, the adapted USEPA method 3051 (HNO_3), which represents acid-extractable concentrations, and the adapted USEPA method 3052 (HNO_3/HF) which provides total elemental concentrations, have been proposed after a series of investigations of various digestion methods for peat material. These digestion methods will be used in the determination of elemental concentrations in peat material in this research project. They will be used as reference methods in the certification of ombrotrophic peat reference materials. They are called (1) the adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat and (2) adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat. The full details of these digestion methods are given in Appendix A.

3.3 Refinement and application of methods to ombrotrophic peat samples

3.3.1 Determination of vertical profiles of elements in a previously collected ombrotrophic peat core by using the two different digestion procedures

The two harmonised digestion procedure protocols were applied to the analyses of elemental concentrations in ombrotrophic peat. This experiment determined and compared the elemental concentrations so obtained for an ombrotrophic peat core collected on 8th July 1999 by monolith (15 cm x 7 cm x 50 cm) from Flanders Moss. The following observations were made during collection; 0-19 cm, a gradual reduction in vegetation; 19-22 cm, a significant increase in peat material; 23-25 cm, colour changed from light brown to dark brown; 25-43 cm, high peat content with

dark brown/black colour. The wet weight, air-dried weight, wet/dry weight ratio, water content (% by weight), and ash contents (expressed relative to the dry weight at 105°C) are shown for each 1-cm section in Table 3.10. This information and the generated elemental concentration data were also used for subsequent assessment of the depth of peat material to be collected for the production of the certified reference material.

3.3.1.1 Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat (total-recoverable digestion method)

Approximately 0.250 g dried ombrotrophic peat sample was accurately weighed out. The Canadian peat OGS 1878 P-6 reference material was analysed for quality control purposes in each analysis batch. These samples were placed in Pyrex beakers in a muffle furnace for four hours at 100°C, and for a further four hours at 450°C. After the samples had cooled down, each was placed in a Teflon microwave digestion vessel with 10 ml ARISTAR HNO_3 and then digested in a CEM MARS 5 microwave digestion system. The programme used had the following features: Temperature control, Maximum power 1200 W, 100%, Phase 1-ramp to 165°C, 3.0 mins, Phase 2-ramp to 175°C, 2.5 mins, hold at 175°C 10 mins. Upon cooling, the samples were filtered through Whatman No. 542 filter paper to remove any remaining solid material. The solutions were evaporated down to approximately 1 ml on a hotplate and then made up to 25 ml with 2% v/v ARISTAR HNO_3. The sample solutions were finally analysed for Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, S, Sb, Se, P, Pb, Ti, V, and Zn by ICP-OES.

3.3.1.2 Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat (total-total digestion method)

Approximately 0.250 g dried ombrotrophic peat sample was accurately weighed out. The Canadian peat OGS 1878 P-6 reference material was analysed for quality control purposes in each analysis batch. These samples were placed in Pyrex beakers in a muffle furnace for four hours at 100°C, and for a further four hours at 450°C. After the samples had cooled down, each was placed in a Teflon microwave digestion vessel with 9 ml ARISTAR HNO_3, and 0.5 ml of ARISTAR HF, and then digested in

a CEM MARS 5 microwave digestion system. The programme used had the following features: Temperature control, Maximum power 1200 W, 100%, Phase 1-ramp to 175°C, 3.0 mins, Phase 2-ramp to 180°C, 2.5 mins, hold at 180°C 9.5 mins. Upon cooling, the samples were transferred to 100 ml Teflon beakers. The solutions were evaporated down to approximately 1 ml on a hotplate and then made up to 25 ml with 2% v/v ARISTAR HNO_3. The sample solutions were finally analysed for Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, S, Sb, Se, P, Pb, Ti, V, and Zn by ICP-OES.

3.3.1.3 ICP-OES analysis

The determination of elemental concentrations in the digested peat samples was carried out by ICP-OES (Tables 3.1 and 3.2). The following concentrations of standard solutions for major elements were used in construction of the calibration curve: 6.25 mg/l, 12.50 mg/l, 25.00 mg/l, and 50.00 mg/l prepared in 2% v/v HNO_3. For trace elements, the following concentrations of standard solutions were used: 0.25 mg/l, 0.50 mg/l, 1.00 mg/l, and 2.00 mg/l prepared in 2% v/v HNO_3.

3.3.1.4 Results and discussion

This experiment compared the concentrations of inorganic elements in the ombrotrophic peat core obtained from the acid-extractable (HNO_3) and total digestion (HNO_3/HF) methods. The elemental concentrations are shown in Table 3.11 and Table 3.12. These results demonstrated that, for major elements (i.e. Al, Ti) and some trace elements (i.e. Co, Cr), total elemental concentrations are higher than the acid-extractable elemental concentrations. This finding was in accord with the previous study using Canadian peat OGS 1878 P-6.

Table 3.10 Section wet weight, air-dried weight, wet/dry weight ratio, water content (% by weight), and ash content (expressed relative to the dry weight at 105°C) of Flanders Moss peat core collected in 1999.

Sample depth (cm)	Wet weight (g)	Air-dried weight (g)	Wet/dry weight ratio	Water content by weight (%)	Ash content (%)
0-2	18.46	4.60	4.01	75.1	1.72
2-3	16.21	3.63	4.47	77.6	1.77
3-4	18.69	3.86	4.84	79.3	1.55
4-5	87.62	13.55	6.47	84.5	1.99
5-6	36.93	5.32	6.94	85.6	0.89
6-7	54.27	5.77	9.41	89.4	1.11
7-8	41.27	5.00	8.25	87.9	0.88
8-9	54.27	6.31	8.60	88.4	1.11
9-10	107.11	13.72	7.81	87.2	0.90
10-11	87.59	8.97	9.76	89.8	0.68
11-12	50.46	5.44	9.28	89.2	1.16
12-13	92.79	10.00	9.28	89.2	0.71
13-14	80.59	9.75	8.27	87.9	0.92
14-15	80.26	9.80	8.19	87.8	1.86
15-16	79.00	8.94	8.84	88.7	0.71
16-17	86.63	9.45	9.17	89.1	0.93
17-18	170.61	21.37	7.98	87.5	2.28
18-19	107.99	13.69	7.89	87.3	1.41
19-20	140.02	15.25	9.18	89.1	2.95
20-21	173.72	18.39	9.45	89.4	2.77
21-22	114.11	7.80	14.63	93.2	3.45
22-23	91.08	6.19	14.71	93.2	2.52
23-24	161.51	11.70	13.80	92.8	4.35
24-25	86.88	10.68	8.13	87.7	5.25
25-26	113.56	15.94	7.12	86.0	6.04
26-27	155.67	23.73	6.56	84.8	6.03
27-28	108.24	19.40	5.58	82.1	7.17
28-29	110.28	19.02	5.80	82.8	5.25
29-30	123.92	20.11	6.16	83.8	5.59
30-31	86.54	14.00	6.18	83.8	3.47
31-32	89.91	13.96	6.44	84.5	4.41
32-33	135.35	19.03	7.11	85.9	5.07
33-34	97.11	13.88	7.00	85.7	5.15
34-35	116.71	15.89	7.34	86.4	2.07
35-36	103.46	12.93	8.00	87.5	1.60
36-37	86.31	10.44	8.27	87.9	1.36
37-38	71.48	8.79	8.13	87.7	2.25
38-39	99.39	12.06	8.24	87.9	0.70
39-40	104.45	11.75	8.89	88.8	1.82
40-41	146.72	13.90	10.56	90.5	1.55
41-42	83.52	7.63	10.95	90.9	1.33
42-43	122.05	9.30	13.12	92.4	1.37

Table 3.11 Elemental concentrations in a Flanders Moss peat core prepared for analysis according to "adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat".

Elements/Depth (cm)	Concentration (mg/kg)[a]															
	Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	P	Pb	S	Ti	V	Zn
0-2	139	3256	0.06	<0.5*	4.6	189	769	200.6	989	4.4	510	4.3	623	6.8	0.8	115
2-3	200	3823	<0.5*	<0.5*	5.4	216	971	285.0	764	1.7	564	<2.8*	709	9.4	1.3	196
3-4	187	3645	0.09	<0.5*	5.3	240	846	218.3	1162	3.5	564	6.4	709	8.5	0.6	258
4-5	222	2895	0.09	<0.5*	4.9	244	794	166.6	872	1.7	450	3.5	627	8.4	1.3	305
5-6	239	2253	0.34	<0.5*	4.3	266	705	95.5	356	1.8	367	1.2	494	9.3	1.8	183
6-7	269	2196	0.32	<0.5*	4.1	264	740	71.9	404	0.8	345	<2.8*	923	9.8	1.8	328
7-8	368	1870	0.39	<0.5*	3.9	292	746	67.1	401	1.7	354	1.3	448	11.8	2.5	197
8-9	294	1719	0.10	0.23	2.9	270	714	74.5	411	4.1	323	8.6	428	10.7	2.4	263
9-10	357	1465	0.25	0.18	3.3	328	755	37.1	376	1.2	305	1.8	421	13.3	2.3	240
10-11	392	1451	0.40	0.44	4.0	365	827	33.3	508	11.2	288	7.1	433	13.6	3.1	261
11-12	419	1363	0.44	0.47	3.9	412	892	15.4	477	2.2	283	8.8	536	15.7	2.4	234
12-13	406	1310	0.22	0.23	3.6	406	907	22.4	408	0.3	275	11.5	414	14.5	3.3	224
13-14	470	1214	0.47	0.28	4.0	531	952	12.5	315	2.3	256	19.9	408	20.3	4.6	223
14-15	480	1309	0.75	0.34	5.3	678	998	15.1	330	1.7	271	29.3	411	20.3	4.0	337
15-16	474	1214	0.66	0.72	4.4	786	996	49.6	298	3.0	297	40.2	447	18.5	4.1	337
16-17	529	1185	0.86	0.09	5.1	1107	1045	24.5	313	4.6	298	39.8	577	18.3	4.0	288
17-18	599	1250	1.07	<0.5*	6.1	1456	1147	18.1	337	3.2	316	56.3	697	20.2	4.4	334
18-19	760	1426	1.35	0.62	6.4	2599	1215	20.0	378	5.3	418	82.0	801	27.4	6.3	213
19-20	711	1374	1.16	0.54	6.9	2476	1169	14.9	290	5.8	435	77.7	598	26.3	6.1	277
20-21	748	1464	1.36	1.30	7.8	2558	1151	23.6	318	4.8	461	89.1	702	28.7	5.9	247
21-22	1035	1737	1.00	2.20	10.5	2243	1243	13.1	342	5.8	604	107.5	794	38.3	8.3	320
22-23	973	1359	1.40	3.05	9.0	2537	1201	13.8	346	6.0	603	104.3	724	36.4	8.9	224
23-24	1446	1400	1.46	4.79	12.3	2376	1100	15.3	305	7.6	736	129.8	995	58.0	11.1	251
24-25	2444	1677	1.52	6.00	25.0	1212	967	9.4	254	10.5	600	185.6	1153	100.2	14.9	131
25-26	2639	1257	1.61	7.16	28.1	935	905	8.8	248	10.4	489	203.0	1324	114.7	17.1	109
26-27	3009	1081	1.48	5.89	18.5	834	768	5.9	268	8.5	367	191.3	987	147.0	15.9	91
27-28	3140	901	1.54	5.07	11.5	669	669	4.3	225	6.0	282	167.7	813	144.0	14.1	63
28-29	2605	837	0.97	2.14	4.7	541	621	2.1	203	4.8	251	112.7	733	92.6	9.0	63
29-30	2811	879	1.01	3.08	5.3	599	656	2.6	194	6.2	268	128.4	794	106.4	9.3	93
30-31	2581	793	0.69	1.79	1.8	546	615	2.1	164	4.1	251	86.6	646	91.9	7.3	49
31-32	2496	814	0.78	2.11	1.4	560	634	2.1	191	4.5	241	70.7	640	86.5	6.4	76
32-33	2587	776	0.82	1.90	1.2	582	621	2.3	194	8.0	240	70.2	573	88.2	6.0	102
33-34	2550	728	0.67	2.05	0.5	536	575	2.0	171	7.1	223	47.6	517	82.3	5.9	81
34-35	1953	944	0.83	0.65	1.0	595	744	1.8	233	5.2	200	35.9	704	64.2	4.1	72
35-36	1868	1097	0.90	0.61	1.7	674	898	2.0	215	3.8	192	30.9	790	58.6	3.4	116
36-37	1590	1092	0.58	0.70	0.8	652	940	1.6	415	2.7	180	30.9	781	59.0	3.1	121
37-38	1619	1127	0.70	0.26	2.4	662	1022	1.5	249	3.2	187	22.4	726	68.6	2.2	59
38-39	1582	1157	1.03	0.49	2.3	714	1067	2.0	230	4.0	171	17.8	775	83.4	2.7	158
39-40	1306	1133	0.89	0.48	1.9	654	1102	2.2	237	2.8	141	15.0	701	78.7	1.7	139
40-41	1032	1067	0.56	0.13	2.5	606	1097	1.2	223	1.5	138	11.9	769	57.1	1.8	191
41-42	1153	1302	0.51	0.20	3.0	745	1292	1.4	280	3.1	158	8.3	910	64.2	2.1	124
42-43	867	1006	0.43	0.04	3.7	649	1063	1.8	253	1.7	144	15.6	729	47.3	1.6	331

[a] All concentration data are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat. *Lower than limit of detection (Table 3.2).

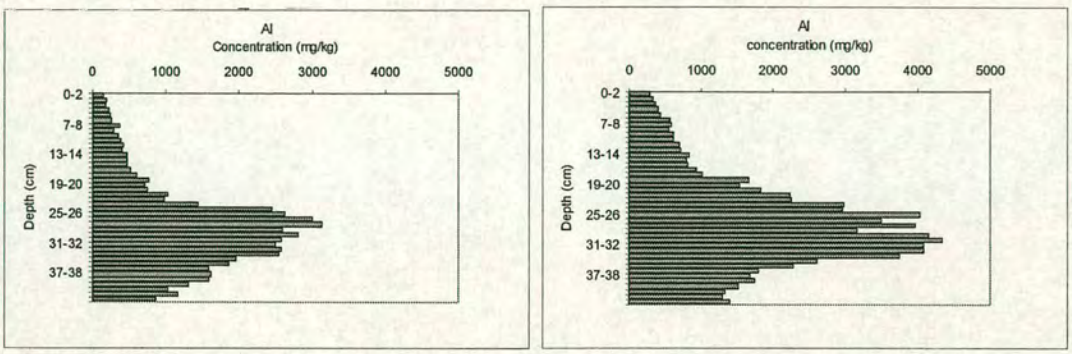
Table 3.12 Elemental concentrations in a Flanders Moss peat core prepared for analysis according to "adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".

Elements/Depth (cm)	Concentration (mg/kg)[a]															
	Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	P	Pb	S	Ti	V	Zn
0-2	278	3853	0.33	<0.5*	4.4	226	875	251.4	1123	1.6	589	13.0	680	25	1.6	127
2-3	339	4076	0.45	<0.5*	4.7	234	982	275.8	842	2.1	557	6.1	672	25	2.1	181
3-4	373	3515	0.13	<0.5*	4.6	220	842	211.2	1129	2.3	527	3.2	656	25	1.8	251
4-5	393	3170	0.40	0.09	4.8	276	809	166.3	886	2.0	450	7.5	626	28	2.4	329
5-6	437	2282	0.39	0.27	4.9	489	728	102.1	373	0.9	362	2.2	491	31	3.0	206
6-7	564	2155	0.04	0.28	3.9	305	722	76.1	420	1.8	333	8.7	476	34	3.2	359
7-8	580	1981	0.44	1.28	3.9	340	761	53.4	535	1.2	346	4.6	804	44	3.2	203
8-9	553	1860	0.15	0.36	3.4	327	738	47.9	624	1.6	303	8.5	497	37	2.9	290
9-10	613	1509	0.23	0.58	3.5	421	730	58.0	472	1.8	313	11.4	390	42	3.3	227
10-11	622	1479	0.56	0.65	3.1	390	812	22.3	560	1.2	274	14.4	393	43	3.3	278
11-12	695	1364	0.62	0.86	3.2	471	876	20.0	515	1.5	256	15.4	365	48	4.2	258
12-13	715	1318	0.60	0.74	3.4	478	905	17.0	516	1.4	250	19.5	412	51	4.3	228
13-14	830	1234	0.64	1.33	2.6	614	993	11.9	385	4.4	270	33.5	396	89	6.0	229
14-15	795	1438	1.08	1.46	5.0	771	1075	35.5	433	5.1	306	42.3	402	61	5.7	354
15-16	812	1261	0.58	1.41	5.6	942	1090	21.4	356	3.5	327	47.1	454	60	5.0	362
16-17	939	1321	0.96	1.53	5.0	1339	1135	22.3	406	2.5	325	59.6	667	60	6.2	338
17-18	1010	1253	1.24	1.54	5.1	1565	1139	26.8	375	4.0	326	72.2	659	62	6.0	344
18-19	1660	1536	1.53	2.46	5.9	2989	1258	23.0	479	5.7	442	100.8	796	104	8.8	220
19-20	1538	1441	1.62	3.18	6.3	2756	1274	17.6	427	5.0	475	99.0	657	93	8.5	309
20-21	1826	1576	1.87	3.46	6.6	3270	1313	24.8	474	4.8	540	109.5	809	111	10.2	319
21-22	2233	1513	1.85	6.26	7.5	2602	1220	14.2	509	6.4	618	133.9	851	133	11.5	358
22-23	2251	1363	2.02	6.37	7.7	2904	1185	15.9	476	6.2	616	120.4	717	141	11.9	217
23-24	2982	1390	2.76	10.72	10.6	2945	1048	21.4	579	11.0	766	138.6	1038	236	18.0	249
24-25	2971	463	2.98	16.44	19.0	1411	243	12.8	655	14.8	619	201.1	1213	377	23.0	153
25-26	4038	400	3.32	11.31	24.3	1200	298	13.6	700	16.3	533	226.0	1180	468	27.1	123
26-27	3496	269	2.79	9.05	12.9	965	160	9.9	765	10.5	368	193.5	993	513	23.1	92
27-28	3959	387	2.52	6.85	3.4	834	332	8.4	876	9.4	303	179.9	875	569	21.4	62
28-29	3163	398	2.13	5.96	9.0	709	299	6.4	826	6.7	228	119.0	746	455	16.6	72
29-30	4155	894	2.02	5.85	9.8	793	590	6.4	754	4.9	268	130.3	779	501	16.6	99
30-31	4333	860	1.68	4.97	4.9	716	667	5.5	762	3.9	262	91.3	566	477	14.5	58
31-32	4091	891	1.54	3.99	3.9	713	693	5.0	688	3.6	255	79.0	693	429	12.5	81
32-33	4088	823	1.67	4.24	3.6	709	646	5.4	759	3.9	254	64.1	550	463	13.7	114
33-34	3755	790	1.54	4.16	2.9	721	588	5.5	767	2.9	227	52.9	581	450	12.8	90
34-35	2622	1002	1.19	2.08	2.7	687	849	3.0	410	4.2	211	41.6	748	230	6.3	79
35-36	2279	1048	1.25	1.92	2.0	705	888	2.8	306	3.1	207	34.9	765	169	5.0	139
36-37	1802	1100	0.89	1.12	1.9	724	959	2.2	291	1.8	185	22.8	848	128	3.7	119
37-38	1677	1125	1.00	0.81	1.3	756	997	2.0	331	2.4	195	22.3	784	133	4.4	69
38-39	1754	1178	1.03	1.13	0.4	799	1077	2.4	290	1.6	180	23.6	795	156	4.4	160
39-40	1511	1225	0.95	0.72	0.5	761	1195	2.6	348	1.9	164	21.6	824	145	3.8	158
40-41	1332	1225	1.10	0.37	1.8	783	1303	1.6	329	2.4	172	15.3	946	100	3.4	201
41-42	1296	1276	0.86	0.46	1.9	760	1318	1.6	323	0.7	160	16.8	936	96	3.3	126
42-43	1405	1285	0.95	1.14	1.9	846	1381	2.7	373	2.0	182	25.5	946	105	3.8	414

[a] All concentration data are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat. *Lower than limit of detection (Table 3.2).

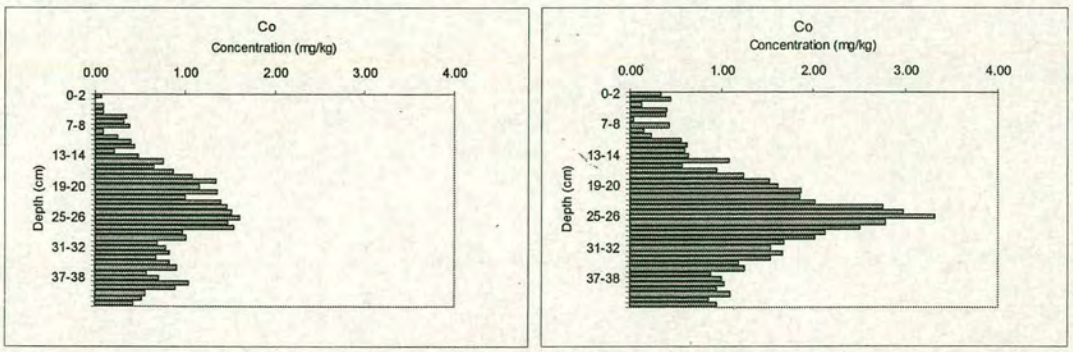
3.3.1.5 Comparison of the vertical profiles of elements in the 1999 Flanders Moss ombrotrophic peat core

The vertical profiles of elements obtained from these two digestion methods are shown in Figs 3.4 – 3.16.



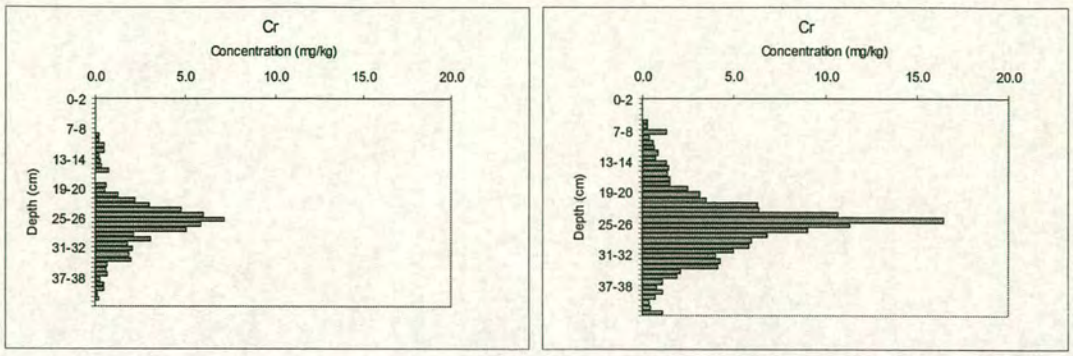
(a) (b)

Figure 3.4 Vertical profile of Al in peat core (a) prepared for analysis according to "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat" comparing with (b) prepared for analysis according to "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".



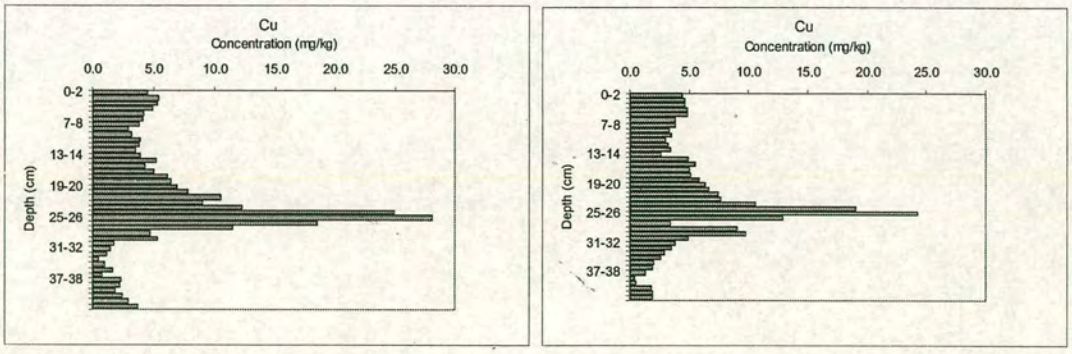
(a) (b)

Figure 3.5 Vertical profile of Co in peat core (a) prepared for analysis according to "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat" comparing with (b) prepared for analysis according to "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".



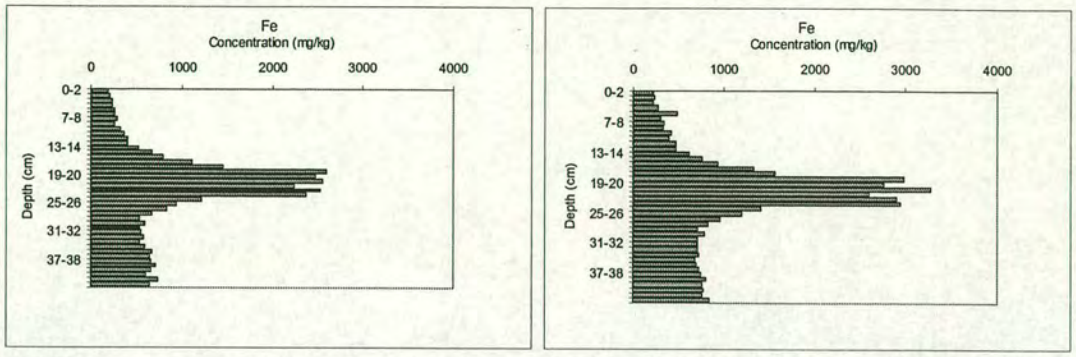
(a) (b)

Figure 3.6 Vertical profile of Cr in peat core (a) prepared for analysis according to "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat" comparing with (b) prepared for analysis according to "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".



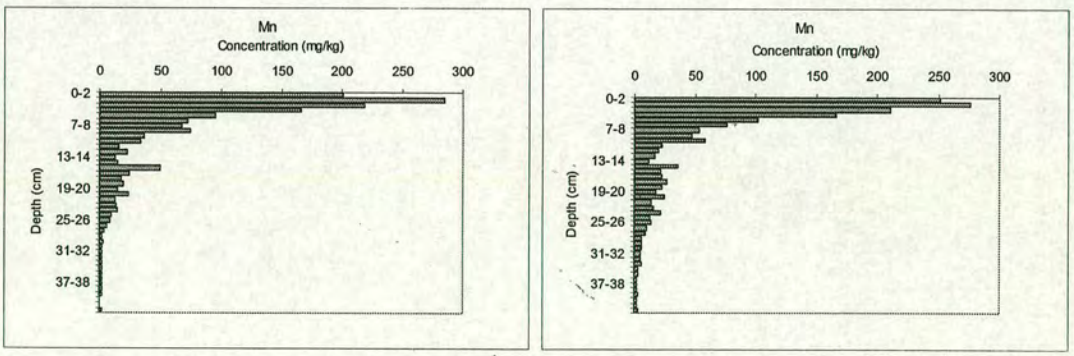
(a) (b)

Figure 3.7 Vertical profile of Cu in peat core (a) prepared for analysis according to "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat" comparing with (b) prepared for analysis according to "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".



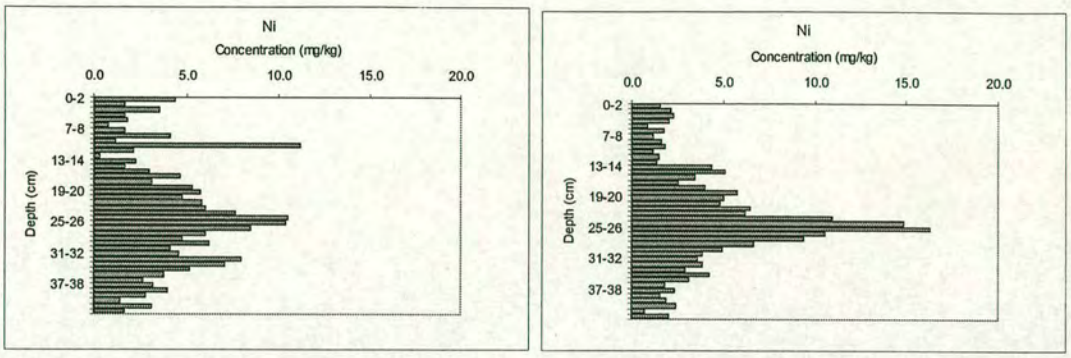
(a) (b)

Figure 3.8 Vertical profile of Fe in peat core (a) prepared for analysis according to "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat" comparing with (b) prepared for analysis according to "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".



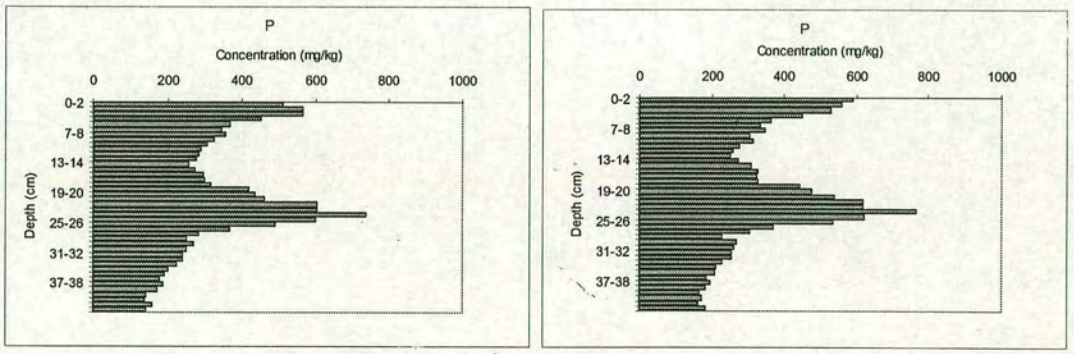
(a) (b)

Figure 3.9 Vertical profile of Mn in peat core (a) prepared for analysis according to "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat" comparing with (b) prepared for analysis according to "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".



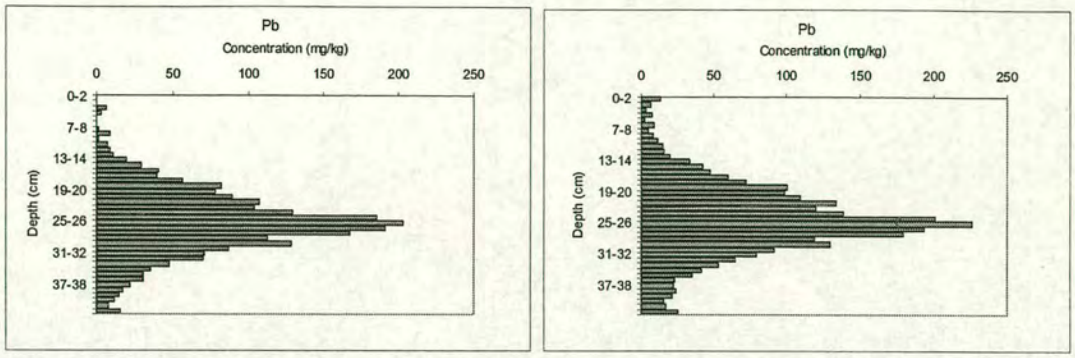
(a) (b)

Figure 3.10 Vertical profile of Ni in peat core (a) prepared for analysis according to "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat" comparing with (b) prepared for analysis according to "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".



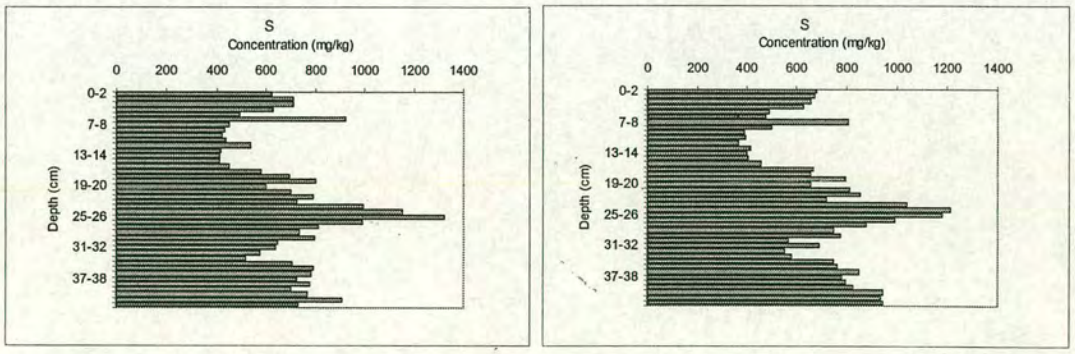
(a) (b)

Figure 3.11 Vertical profile of P in peat core (a) prepared for analysis according to "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat" comparing with (b) prepared for analysis according to "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".



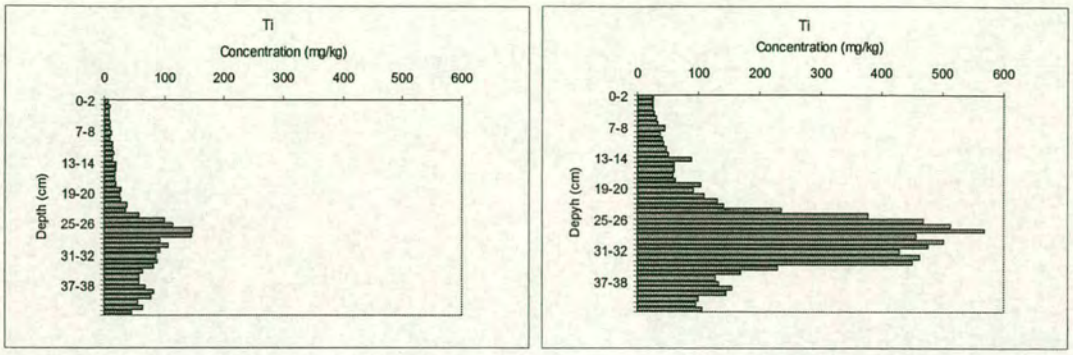
(a) (b)

Figure 3.12 Vertical profile of Pb in peat core (a) prepared for analysis according to "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat" comparing with (b) prepared for analysis according to "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".



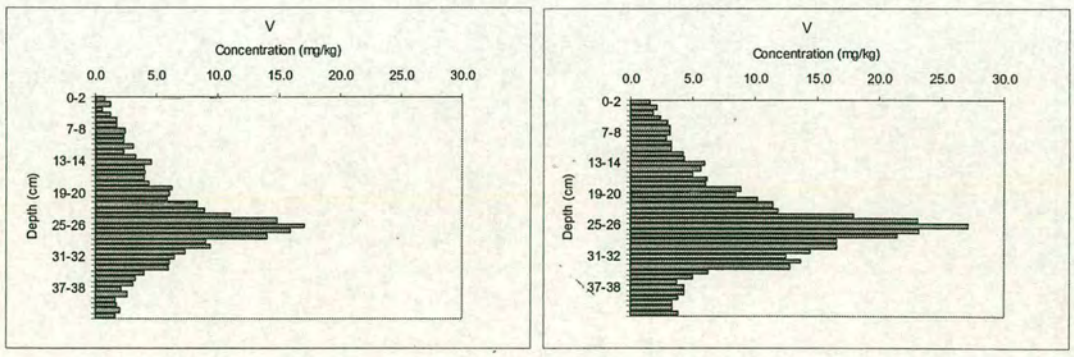
(a) (b)

Figure 3.13 Vertical profile of S in peat core (a) prepared for analysis according to "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat" comparing with (b) prepared for analysis according to "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".



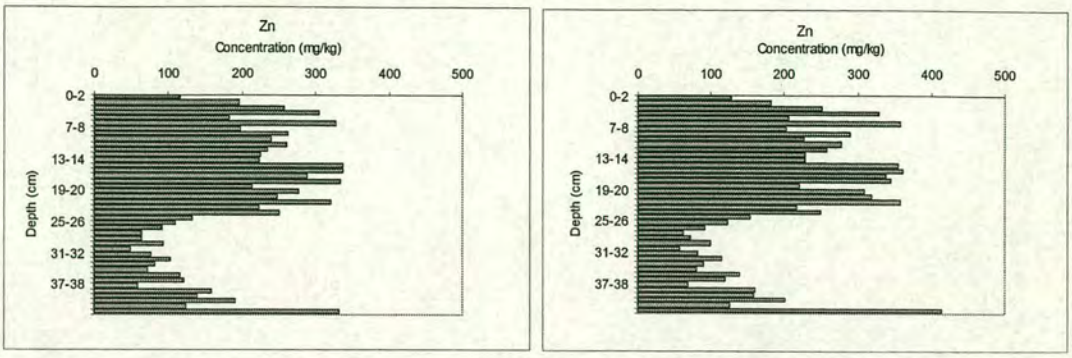
(a) (b)

Figure 3.14 Vertical profile of Ti in peat core (a) prepared for analysis according to "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat" comparing with (b) prepared for analysis according to "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".



(a) (b)

Figure 3.15 Vertical profile of V in peat core (a) prepared for analysis according to "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat" comparing with (b) prepared for analysis according to "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".



(a) (b)

Figure 3.16 Vertical profile of Zn in peat core (a) prepared for analysis according to "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat" comparing with (b) prepared for analysis according to "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat".

From Figs 3.4 - 3.16, it can be seen that vertical concentration profiles of metals in this peat core obtained from the acid-extractable digestion method (HNO_3) are similar in shape and trend to those obtained from the total digestion method (HF/HNO_3), but total concentrations are clearly higher than acid-extractable concentrations for some major elements (i.e. Al, Fe, and Ti) and some trace elements (i.e. Co, Cr, Ni, and V). The other trace element results, however, demonstrate the capability of HNO_3 for sample preparation of ombrotrophic peat material.

The interpretation of these vertical profiles of inorganic elements in this Flanders Moss peat core will be discussed later in Chapter 6.

3.3.1.6 Conclusions

From this experiment we can conclude that both total and acid-extractable digestion methods generate similarly shaped vertical profiles of elemental concentrations in this Flanders Moss ombrotrophic peat core. However, total concentrations of some major elements such as Al and Ti are clearly higher than acid-extractable concentrations. Also, it was discovered that peat from a depth of ~ 20 - 40 cm should be collected from Flanders Moss in order to have reasonably high elemental concentrations in the intended ombrotrophic peat reference material.

In summary, it is necessary to use HF in the digestion of peat material to achieve total elemental concentrations, especially for major elements and some trace elements such as Cr and V. Two microwave-assisted digestion methods, the adapted USEPA method 3051 (HNO_3), which represents acid-extractable concentrations, and the adapted USEPA method 3052 (HNO_3/HF), which provides total elemental concentrations, have been proposed after a series of investigations of various digestion methods for peat material. These digestion methods will be used in the determination of elemental concentrations in peat material in this research project. For the production of ombrotrophic peat material, the starting material will be collected from Flanders Moss at a depth of 20 – 40 cm.

Chapter 4

Development of Ombrotrophic Peat Bog Reference Material

Reference materials play an important role in the evaluation of the accuracy of analytical results, and are essential parts of good laboratory practice. A peat reference material would be very important in establishing traceability and accuracy in the study of past atmospheric metal deposition using peat from ombrotrophic bogs. Given the increase in this type of study, the lack of a common, validated sample preparation method and of a certified peat reference material has hindered not only the quality assurance of the generated analytical data but also the interpretation and comparison of peat core metal profiles from different laboratories in the international community. Plant and soil certified reference materials (CRMs) have been used for quality control in this type of study instead of a peat reference material. In addition, different laboratories in this field of research currently adopt a wide range of practices, including the determination of acid-extractable and of total elemental concentrations by various instrumental analytical techniques. To compare and standardise these different approaches, we developed a new candidate peat reference material, derived from an ombrotrophic bog, and subjected it to an international inter-laboratory comparison exercise as part of the certification process.

This chapter can be divided into five parts; preparation of the candidate ombrotrophic peat bog reference material, preliminary homogeneity study of the bulk candidate material, homogeneity testing of the candidate material, stability testing of the candidate material, and characterisation and certification of the candidate ombrotrophic peat bog reference material.

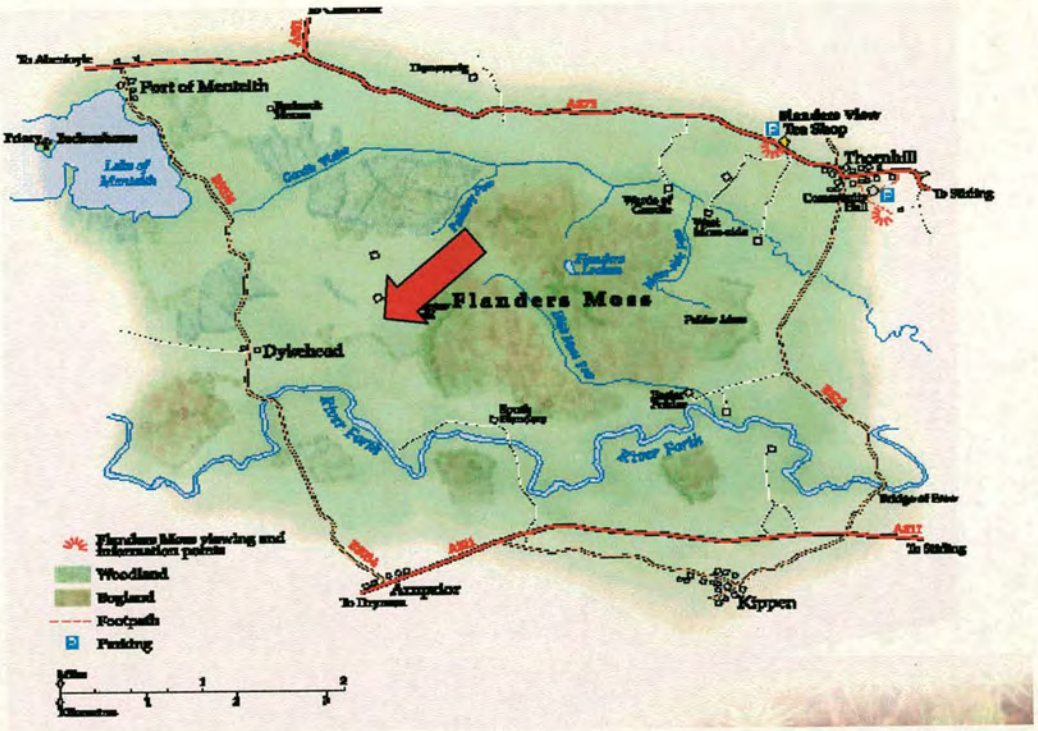
4.1 Physical preparation of candidate ombrotrophic peat bog reference material

4.1.1 Collection of starting material

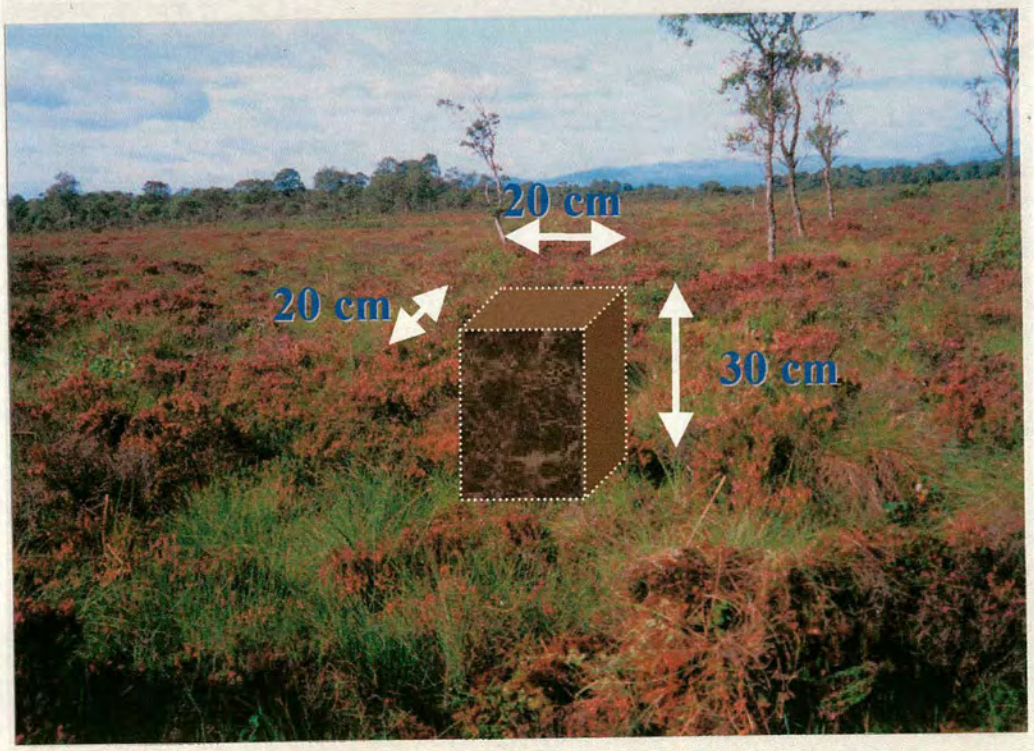
On 11 September, 2001, the starting material was collected from the ombrotrophic peat bog at Flanders Moss, near Stirling, Scotland (Fig. 4.1(a)). Vegetation on top of the bog was removed using a stainless steel knife and the peat sample dug up by a spade from a depth of ~ 30 cm in blocks of approximate size 20 cm x 20 cm x 30 cm (Fig. 4.1(b)). Seven blocks of peat of about the same size were collected, yielding a total wet weight of ~ 70 kg. The wet peat was wrapped up in a polyethylene bag and transported to the Macaulay Institute, Aberdeen, UK, the following day.

4.1.2 Physical treatment of starting material

The wet peat material was then divided into sub-samples, from which root material was extracted by hand, and air-dried at 30°C for 10 days on paper-lined aluminium trays. The dried peat was then broken into small aggregates with a wooden hammer and air-dried for a further week. Ten sub-samples were then randomly taken from the drying trays. The moisture content based on oven-drying at 105°C was determined on each sub-sample, yielding a mean moisture content of ~ 10% in 30°C air-dried peat. The air-dried peat was milled to less than 2 mm in particle size with a stainless steel hammer mill (Christie Hunt). The milling machine is shown in Fig 4.2. Approximately 4.5 kg of peat material was obtained and transferred into a 20-litre glass jar, which was placed on a roller bed for two weeks. Fig. 4.3 shows the roller bed used for homogenisation.



(a)



(b)

Figure 4.1 Ombrotrophic peat bog at Flanders Moss, near Stirling, Scotland, (a) map, (b) sampling procedure.

Figure 4.2 Stainless steel hammer mill (Christie Hunt).

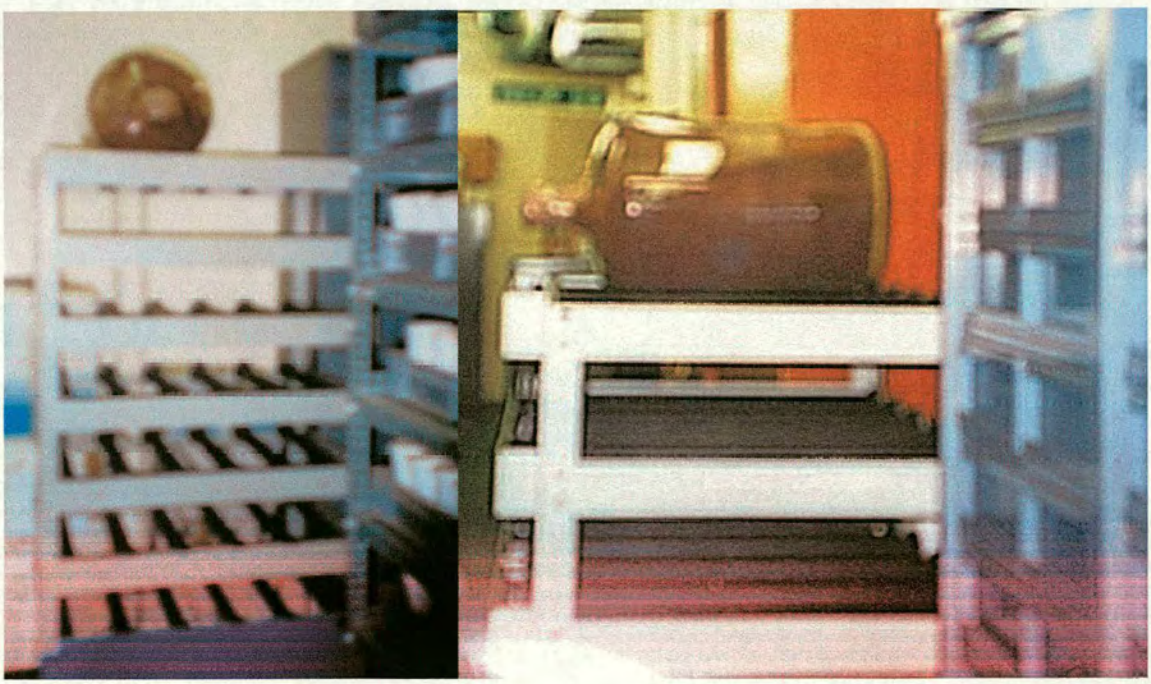


Figure 4.3 The roller bed used for homogenisation.

4.2 Preliminary homogeneity study of bulk candidate ombrotrophic peat bog reference material

Ten sub-samples (~ 2 g each) were randomly taken from the jar and analysed for metal concentrations to make a preliminary assessment of the bulk homogeneity using a modified version of ASTM 826-85 "Standard practice for testing homogeneity of material for development of reference material" (1985). This mainly involved the selection of test sub-samples from the bulk material, digestion and analysis of sub-samples (0.25 g), and statistical treatment of the measurement data using the ASTM 826-85 standard protocol. The total concentration for each element of interest was the variable evaluated to assess homogeneity. The elemental concentrations were determined by ICP-OES after samples were digested using the adapted USEPA method 3052 microwave-assisted HF/HNO_3 digestion of peat (total digestion method) (Section 3.2, Chapter 3).

Using Pb as an example, data for total Pb concentration in the preliminary homogeneity testing of the candidate ombrotrophic peat (low ash) reference material are displayed in Table 4.1.

Table 4.1 Data for total Pb concentration (mg/kg) (dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat) in the preliminary homogeneity testing of the candidate ombrotrophic peat (low ash) reference material.

replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	154	172	168	164	164	170	165	174	164	175	B_1 = 1672
2	175	188	169	163	164	169	163	172	163	180	B_2 = 1705
3	173	168	169	165	172	162	178	164	185	166	B_3 = 1703
Total	T_1=501	T_2=528	T_3=506	T_4=493	T_5=500	T_6=501	T_7=507	T_8=511	T_9=512	T_9=521	G= 5080
Mean	t'_1=167	t'_2=176	t'_3=169	t'_4=164	t'_5=167	t'_6=167	t'_7=169	t'_8=170	t'_9=171	t'_9=174	

The measurement results (Table 4.1) were treated as follows.

- *T, B, t'*, and *G* were computed, where: *T* = sum of each column; *B* = sum of each row; *t'* = mean of each column; and *G* = sum of $B_1 \ldots B_n$; *b* = number of

replicate measurements from different aliquots of the solid material (3); and t = number of sub-samples (10)

- The degree of freedom at 95% confidence level was calculated from:

  $\nu = (b-1)(t-1)$, where ν = the number of degrees of freedom

  $\nu = 18$

- The value of symbol q corresponding to t and ν was found from the reference table given in ASTM 826-85.

  $q = 5.07$

- The sum of squares due to the sub-samples, S_t, was calculated from

  $S_t = [(T_1^2 + T_2^2 + \ldots T_t^2)/b] - (G^2/tb) = 341$

- The sum of squares due to runs, S_b, was calculated from

  $S_b = [(B_1^2 + B_2^2 + \ldots B_t^2)/t] - (G^2/tb) = 69$

- The sum of squares of all the measurements in Table 4.1, $S_{average}$, was defined and calculated from

  $S_{average} = (\sum_{i=1}^{t})(\sum_{j=1}^{b}) Y_{ij}^2 - (G^2/tb)$, where Y_{ij} = individual values in Table 4.1.

  $S_{average} = 1491$

- The symbol s was defined and calculated from

  $s = \sqrt{(S_{average} - S_b - S_t)/(b-1)(t-1)} = 7.8$

- The symbol w was defined and calculated from

  $w = qs/\sqrt{b} = 23$

The maximum and minimum of the mean t' values in Table 4.1 are 176 and 164, respectively, so the maximum difference between any of the mean t' values in Table 4.1 is 12. As the absolute difference between any two mean values does not exceed w (= 23), then there is strong evidence, at 95% confidence level, that the bulk material is homogeneous for Pb.

The same calculation was applied to Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, P, S, Ti, V, and Zn, for which similar satisfactory evidence of homogeneity was obtained in each case (Table 4.2). Full details of raw data in this preliminary study for each element are shown in Appendix B.

Table 4.2 Preliminary assessment of the bulk homogeneity using a modified version of ASTM 826-85 for Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, P, S, Ti, V, and Zn.

Element	v	q	S_t	S_b	$S_{average}$	S	w	d	D < w	Conclusion
Al	18	5.07	1308366	336720	3369450	300	879	744	Yes	homogeneous
Ca	18	5.07	6927	1771	26026	31	91	44	Yes	homogeneous
Co	18	5.07	0.14	0.0067	0.663	0.169	0.49	0.21	Yes	homogeneous
Cr	18	5.07	4.03	0.0058	9.46	0.55	1.61	1.25	Yes	homogeneous
Cu	18	5.07	8.05	2.64	36.78	1.20	3.52	1.00	Yes	homogeneous
Fe	18	5.07	1834	152	6864	17	48	30	Yes	homogeneous
Mg	18	5.07	72287	10814	159584	65	191	176	Yes	homogeneous
Mn	18	5.07	0.29	0.06	1.34	0.23	0.68	0.41	Yes	homogeneous
P	18	5.07	1515	214	5806	15	44	23	Yes	homogeneous
S	18	5.07	22297	3157	50699	37	110	90	Yes	homogeneous
Ti	18	5.07	9684	459	30493	34	98	62	Yes	homogeneous
V	18	5.07	1.32	0.03	6.15	0.52	1.51	0.76	Yes	homogeneous
Zn	18	5.07	7.1	0.9	25.4	1.0	2.9	1.8	Yes	homogeneous

Following the preliminary homogeneity tests, the peat material was further homogenised by mixing in the jar on the roller bed for another week. The roller bed was then stopped, and peat material was taken from the jar to fill a series of five pre-cleaned amber glass bottles, each containing a minimum of 30 g. After that, they were promptly closed using polyethylene screwcaps. The glass jar was again rotated for another five minutes and the next five bottles were filled in the same way. The cycle was repeated until a total of 145 (29 x 5) bottles of candidate peat reference material were finally obtained. About ten percent of the bulk peat material that was left on the bottom of the jar was discarded, just in case it was less homogeneous. Twenty-nine bottles (one from each series) were set aside for homogeneity and stability testing. The candidate ombrotrophic peat bog reference material was then named NIMT/UOE/FM/001. The ash content (450°C) of this material was ~ 4-5% of the 30°C air-dried weight.

4.3 Homogeneity testing of candidate ombrotrophic peat bog reference material

Homogeneity testing for total and acid-extractable concentrations of elements in the candidate ombrotrophic peat bog reference material was carried out by using the F-test and ANOVA statistical test. Sixteen (three times the cube root of n units) bottles of candidate peat bog reference material were randomly selected from the 29 bottles that had been set aside earlier. As before, the adapted USEPA Method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat (total-total digestion method), was utilised for total element concentrations, while the adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat (total-extractable digestion method), yielded acid-extractable element concentrations (Section 3.2, Chapter 3).

Using total Pb concentration as an example, analytical results for total Pb concentration in the homogeneity testing of the candidate ombrotrophic peat (low ash) reference material, expressed in mg/kg on a dry-weight (at 105°C) basis, are given in Table 4.3a. Using Microsoft Excel™, Table 4.3b displays the associated ANOVA calculation (one-way layout), in which *SS* provides the sum of squares, *df* represents the associated degrees of freedom, and *MS* expresses mean squares, which form the basis for the computation of variation. The *P-value* gives the level for which the calculated F (F_{cal}) equals $F_{critical}$. From Table 4.3b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total Pb concentration.

Table 4.3a Data for total Pb concentration (mg/kg) (dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat) in the homogeneity testing of the candidate ombrotrophic peat (low ash) reference material.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	163	162	157	160	10.1	3
#2	162	160	161	161	0.8	3
#3	165	159	166	164	12.8	3
#4	165	158	159	161	17.1	3
#5	152	159	166	159	48.3	3
#6	159	166	161	162	10.2	3
#7	164	165	164	164	0.3	3
#8	165	162	165	164	3.2	3
#9	157	156	169	161	47.2	3
#10	164	163	161	163	2.6	3
#11	160	152	147	153	41.4	3
#12	158	154	148	153	27.6	3
#13	168	161	166	165	12.0	3
#14	162	165	166	164	4.2	3
#15	169	170	154	164	79.9	3
#16	154	154	169	159	75.8	3

Table 4.3b Analysis of variance (ANOVA) for homogeneity testing of total Pb concentration (mg/kg) in the candidate ombrotrophic peat (low ash) reference material.

Source of variation	*SS*	*Df*	*MS*	F_{cal}	*P-value*	F_{crital}
Between Bottles	575	15	38	1.559	0.142	1.992
Within Bottles	787	32	25			
Total	1362	47				

The same treatment was applied to other elements of interest, in each case demonstrating the homogeneity of the candidate material. Full details of the homogeneity study for both total and acid-extractable concentrations of Al, Ca, Co,

Cu, Fe, Mg, Mn, P, Pb, S, Ti, V, and Zn are given in Appendix C. On the basis of these results, the material was considered to be homogeneous at the level of 0.25 g, the typical 30°C air-dried weight taken for analysis.

4.4 Stability testing of candidate ombrotrophic peat bog reference material

The stability of the candidate peat bog reference material was tested by storing bottles of the candidate reference material at –20°C, +4°C, +20°C, and +40°C for a period of 12 months. After 1, 3, 6 and 12 months, the total and acid-extractable elemental concentrations were determined (in five replicates). The procedures were the same as those used in the homogeneity study. Instability would be detected by comparing the measured element concentrations of samples stored at +4°C, +20°C, +40°C with those of samples stored at -20°C as determined at various times over 12 months. The samples stored at –20°C were used as reference for the samples stored at +4°C, +20°C and +40°C, respectively. The ratios (R_T) of the mean values ($\overline{X}_T$) of five replicate measurements made for samples stored at +4°C, +20°C and +40°C and the mean value ($\overline{X}_{-20°C}$) from the five determinations at -20°C were calculated as:

$$R_T = \overline{X}_T / \overline{X}_{-20°C}$$

The uncertainty U_T was obtained from the coefficient of variation (CV) of five measurements obtained at each temperature:

$$U_T = (CV_T^2 + CV_{-20\,°C}^2)^{1/2} \cdot R_T$$

The ratios R_T and their corresponding uncertainties are displayed in Tables 4.4 and 4.5. The R_T ratio should be 1 in the case of ideal stability but, as slight instability might be expected during long storage times, the value 1 should lie between $R_T - U_T$ and $R_T + U_T$. For greater than 98 % of the measurements made for samples stored at these conditions, the values fell within $R_T \pm U_T$. It was concluded that there was no instability for a storage time of one year under these conditions. As the candidate material is stable under the storage condition of +40°C for one year, it can be assumed that the material may be stable for up to two or three years under the storage condition of +20°C or below. As a result of the stability testing, all of the elements determined were considered to be suitable for certification, provided that the material is stored at typical room temperature or under refrigeration.

Table 4.4 The ratios R_T and their corresponding uncertainties for total elemental concentrations (relative to those at -20°C) in the stability testing of the candidate ombrotrophic peat reference material NIMT/UOE/FM/001 under different storage conditions.

Element	Time (months)	Ratio of total elemental concentrations		
		+4 °C	+20 °C	+40 °C
Al	1	1.04 ± 0.07	1.01 ± 0.06	1.03 ± 0.06
	3	1.01 ± 0.04	1.02 ± 0.03	1.04 ± 0.03
	6	1.02 ± 0.02	1.00 ± 0.01	1.03 ± 0.02
	12	0.98 ± 0.03	0.96 ± 0.03	0.97 ± 0.04
Ca	1	1.02 ± 0.03	1.00 ± 0.03	1.00 ± 0.02
	3	1.00 ± 0.03	1.01 ± 0.03	1.02 ± 0.03
	6	1.00 ± 0.01	1.01 ± 0.01	1.03 ± 0.01
	12	0.98 ± 0.03	0.97 ± 0.02	1.00 ± 0.02
Co	1	1.07 ± 0.07	1.01 ± 0.07	1.02 ± 0.08
	3	0.96 ± 0.09	0.93 ± 0.09	0.95 ± 0.09
	6	1.12 ± 0.21	1.17 ± 0.18	1.22 ± 0.21
	12	0.93 ± 0.09	0.90 ± 0.10	0.93 ± 0.09
Cr	1	1.02 ± 0.05	1.01 ± 0.03	1.03 ± 0.05
	3	1.02 ± 0.08	1.03 ± 0.08	1.05 ± 0.09
	6	1.06 ± 0.09	1.01 ± 0.07	1.06 ± 0.06
	12	0.98 ± 0.14	0.95 ± 0.06	0.99 ± 0.06
Cu	1	0.98 ± 0.09	1.05 ± 0.10	0.95 ± 0.09
	3	0.97 ± 0.09	0.97 ± 0.08	0.96 ± 0.09
	6	1.02 ± 0.04	1.03 ± 0.06	1.03 ± 0.06
	12	0.93 ± 0.10	0.92 ± 0.13	0.93 ± 0.08
Fe	1	1.01 ± 0.02	1.00 ± 0.04	0.99 ± 0.02
	3	1.02 ± 0.03	1.03 ± 0.03	1.02 ± 0.03
	6	1.01 ± 0.03	1.00 ± 0.02	1.01 ± 0.02
	12	0.98 ± 0.02	0.97 ± 0.03	1.00 ± 0.03
Mg	1	1.02 ± 0.03	1.01 ± 0.03	1.02 ± 0.03
	3	1.01 ± 0.03	1.02 ± 0.02	1.02 ± 0.03
	6	0.99 ± 0.04	0.99 ± 0.03	1.02 ± 0.04
	12	0.98 ± 0.03	0.97 ± 0.02	1.00 ± 0.03
Mn	1	0.98 ± 0.03	1.01 ± 0.05	0.98 ± 0.03
	3	1.01 ± 0.04	1.04 ± 0.05	1.02 ± 0.04
	6	1.02 ± 0.02	1.03 ± 0.04	1.05 ± 0.02
	12	0.99 ± 0.03	1.00 ± 0.06	0.99 ± 0.03
Ni	1	1.03 ± 0.06	1.01 ± 0.03	0.99 ± 0.02
	3	1.00 ± 0.05	1.03 ± 0.06	1.01 ± 0.07
	6	1.07 ± 0.30	0.88 ± 0.15	0.89 ± 1.25
	12	1.03 ± 0.14	1.12 ± 0.15	1.14 ± 0.18
P	1	1.03 ± 0.06	0.99 ± 0.07	1.01 ± 0.06
	3	1.01 ± 0.05	1.01 ± 0.04	1.01 ± 0.03
	6	1.01 ± 0.02	1.00 ± 0.02	0.99 ± 0.04
	12	0.97 ± 0.03	0.95 ± 0.03	0.95 ± 0.04
Pb	1	1.01 ± 0.05	0.99 ± 0.04	1.00 ± 0.04
	3	1.02 ± 0.04	1.02 ± 0.03	1.03 ± 0.04
	6	1.02 ± 0.06	1.01 ± 0.06	0.98 ± 0.04
	12	0.99 ± 0.05	0.99 ± 0.06	0.98 ± 0.05
Ti	1	1.04 ± 0.08	1.04 ± 0.11	1.06 ± 0.08
	3	1.01 ± 0.08	1.02 ± 0.09	1.08 ± 0.08
	6	0.99 ± 0.05	1.02 ± 0.05	1.06 ± 0.04
	12	0.97 ± 0.07	0.94 ± 0.06	0.97 ± 0.08
V	1	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
	3	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
	6	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
	12	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Zn	1	1.04 ± 0.06	1.04 ± 0.12	1.01 ± 0.05
	3	0.98 ± 0.07	1.03 ± 0.07	1.04 ± 0.07
	6	1.01 ± 0.02	0.98 ± 0.02	1.01 ± 0.03
	12	0.98 ± 0.04	1.01 ± 0.04	0.98 ± 0.04

Table 4.5 The ratios R_T and their corresponding uncertainties for acid-extractable elemental concentrations (relative to those at -20°C) in the stability testing of the candidate ombrotrophic peat reference material NIMT/UOE/FM/001 under different storage conditions.

Element	Time (months)	Ratio of acid-extractable elemental concentrations		
		+4 °C	+20 °C	+40 °C
Al	1	1.02 ± 0.06	0.98 ± 0.07	0.99 ± 0.06
	3	0.96 ± 0.07	1.04 ± 0.05	1.01 ± 0.04
	6	0.98 ± 0.03	0.95 ± 0.04	0.96 ± 0.03
	12	0.98 ± 0.06	0.97 ± 0.02	0.97 ± 0.06
Ca	1	1.01 ± 0.04	0.98 ± 0.02	0.98 ± 0.02
	3	0.97 ± 0.04	1.02 ± 0.03	1.01 ± 0.02
	6	0.98 ± 0.03	1.03 ± 0.03	1.08 ± 0.03
	12	1.00 ± 0.02	0.98 ± 0.03	1.01 ± 0.03
Co	1	0.92 ± 0.21	1.00 ± 0.16	1.00 ± 0.22
	3	1.05 ± 0.29	1.13 ± 0.27	1.13 ± 0.26
	6	1.01 ± 0.18	0.88 ± 0.25	0.85 ± 0.17
	12	0.87 ± 0.14	1.07 ± 0.20	1.07 ± 0.20
Cr	1	1.00 ± 0.14	0.94 ± 0.10	0.99 ± 0.11
	3	0.98 ± 0.27	1.00 ± 0.22	0.99 ± 0.23
	6	1.05 ± 0.16	0.97 ± 0.11	1.07 ± 0.12
	12	1.03 ± 0.17	0.96 ± 0.11	0.93 ± 0.12
Cu	1	1.10 ± 0.20	0.99 ± 0.16	1.07 ± 0.20
	3	0.95 ± 0.22	0.99 ± 0.07	1.00 ± 0.08
	6	0.99 ± 0.18	1.01 ± 0.06	1.04 ± 0.10
	12	1.01 ± 0.10	1.00 ± 0.12	0.98 ± 0.10
Fe	1	0.99 ± 0.06	0.94 ± 0.06	1.00 ± 0.08
	3	0.94 ± 0.08	1.02 ± 0.11	1.01 ± 0.08
	6	0.98 ± 0.03	1.03 ± 0.02	1.04 ± 0.03
	12	1.00 ± 0.03	0.98 ± 0.02	0.99 ± 0.03
Mg	1	1.01 ± 0.02	0.98 ± 0.02	0.98 ± 0.02
	3	0.99 ± 0.03	1.04 ± 0.04	1.02 ± 0.03
	6	0.99 ± 0.02	0.99 ± 0.01	1.03 ± 0.01
	12	0.99 ± 0.03	0.99 ± 0.03	0.99 ± 0.03
Mn	1	1.00 ± 0.07	0.94 ± 0.06	0.98 ± 0.07
	3	0.99 ± 0.10	1.06 ± 0.10	1.05 ± 0.07
	6	0.99 ± 0.07	1.05 ± 0.06	1.08 ± 0.09
	12	1.03 ± 0.09	1.01 ± 0.09	0.98 ± 0.08
Ni	1	1.01 ± 0.08	1.00 ± 0.06	1.03 ± 0.06
	3	0.98 ± 0.07	1.08 ± 0.09	1.09 ± 0.11
	6	0.95 ± 0.17	0.94 ± 0.23	0.91 ± 1.22
	12	1.02 ± 0.14	0.93 ± 0.17	0.92 ± 0.19
P	1	1.01 ± 0.03	1.01 ± 0.03	0.99 ± 0.03
	3	0.99 ± 0.03	1.04 ± 0.07	0.99 ± 0.02
	6	0.97 ± 0.02	1.00 ± 0.01	1.01 ± 0.03
	12	1.01 ± 0.03	1.01 ± 0.03	1.04 ± 0.04
Pb	1	1.04 ± 0.05	0.98 ± 0.04	1.01 ± 0.04
	3	0.97 ± 0.07	0.99 ± 0.06	0.98 ± 0.06
	6	0.98 ± 0.05	1.03 ± 0.05	1.00 ± 0.06
	12	1.01 ± 0.04	1.00 ± 0.04	1.04 ± 0.04
Ti	1	0.99 ± 0.08	0.99 ± 0.06	0.96 ± 0.07
	3	1.04 ± 0.06	1.05 ± 0.06	1.07 ± 0.08
	6	0.99 ± 0.09	1.01 ± 0.04	1.02 ± 0.07
	12	1.07 ± 0.06	0.97 ± 0.05	1.02 ± 0.13
V	1	1.01 ± 0.04	0.98 ± 0.06	0.98 ± 0.05
	3	0.89 ± 0.08	1.05 ± 0.09	1.05 ± 0.09
	6	1.01 ± 0.09	0.98 ± 0.04	0.94 ± 0.05
	12	0.97 ± 0.07	1.01 ± 0.06	1.03 ± 0.06
Zn	1	1.02 ± 0.09	0.96 ± 0.08	0.94 ± 0.08
	3	1.02 ± 0.07	1.00 ± 0.08	0.98 ± 0.11
	6	0.99 ± 0.04	1.03 ± 0.03	1.05 ± 0.04
	12	0.98 ± 0.03	1.01 ± 0.04	1.04 ± 0.06

4.5 Characterisation and certification of candidate ombrotrophic peat bog reference material

4.5.1 Methods used in the inter-laboratory comparison exercise

An international inter-laboratory comparison exercise was conducted to certify the reference material. Laboratories invited to take part in the certification exercise were those of experienced research groups in this field of study, considered to be well-equipped and employing quality control and quality assurance procedures. The 14 laboratories taking part were requested to verify the quality of their measurements, in particular the validity of calibration (including calibration of balances, volumetric glassware and other tools of relevance). Each participant was supplied with one bottle of prepared candidate peat material NIMT/UOE/FM/001, inter-laboratory documents (Appendix D), which contained the inter-laboratory comparison protocol giving instructions and details of this exercise, two copies of inter-laboratory pro-forma forms (results reporting forms for total and acid-extractable elemental concentration), and examples of digestion methods that could be used (the adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat and adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat). Participants were free to choose analytical methods of which they had previous experience and could therefore be expected to give valid results when applied by an experienced analyst. They were also asked to make a minimum of five independent replicate determinations of each element in the candidate reference material.

On receipt of data from participants, an identification number (Laboratory ID) was assigned to each laboratory. Where there were two separate sets of data, i.e. one for total elemental concentration and another for acid-extractable element concentration, the Laboratory ID for the latter set is not necessarily the same as that for the former set. Seven laboratories reported data for total (HNO_3/HF, HNO_3/HBF_4, $HNO_3/H_2O_2/H_2O/HF$) concentrations, and ten laboratories for acid-extractable (HNO_3, HNO_3/HCl, $HNO_3/HClO_4$) concentrations, using a range of digestion conditions and a variety of analytical techniques (AAS, GFAAS, ICP-OES, ICP-MS), including, in the case of one laboratory, XRF analysis of the solid phase, and, in two others, thermal decomposition AAS for Hg. Full details of raw data submitted by participants are provided in Appendix E. Table 4.6 lists the digestion methods and instrumental analytical techniques used by the participants.

Table 4.6 Digestion methods and instrumental analytical techniques used by participants in the inter-laboratory comparison exercise for NIMT/UOE/FM/001.

Total concentration	Acid-extractable concentration
Lab1- HNO_3/HBF_4 High pressure microwave autoclave, ICP-MS	**Lab1-** HNO_3 Microwave-assisted, ICP-OES
Lab2- $HNO_3/H_2O_2/H_2O$/HF Microwave-assisted, ICP-OES	**Lab2-** HNO_3 Microwave-assisted, HR-ICP-MS
Lab3- HNO_3/HF Pressure digestion, ICP-MS	**Lab3-** HNO_3 High-pressure ashing, ICP-MS, HG-AAS
Lab4- XRF	**Lab4-** HNO_3 Microwave-assisted (USEPA Method 3051 Protocol), ICP-OES, GFAAS
Lab5- HNO_3/HF Total digestion, ICP-OES	**Lab5-** Aqua regia reflux digestion, ICP-OES
Lab6- HNO_3/HF Microwave-assisted (USEPA Method 3052 Protocol), ICP-OES, GFAAS	**Lab6-** HNO_3 Microwave-assisted (USEPA Method 3051 Protocol), GFAAS, ICP-OES
Lab7- HNO_3/HF Microwave-assisted (USEPA Method 3052 Protocol), ICP-MS	**Lab7-** Aqua-regia digestion (HNO_3, HCl RT 24 hrs, 100 °C , 1 hr, ICP-MS, ICP-OES
Lab8- Thermal decomposition AAS (for Hg only)	**Lab8-** Aqua-regia digestion @125 °C, 3 hrs, FAAS
Lab9- Thermal decomposition AAS (for Hg only)	**Lab9-** $HNO_3/HClO_4$, Heating, ICP-OES
	Lab10- HNO_3 Microwave-assisted (USEPA Method 3051 Protocol), ICP-MS

4.5.2 Results of the inter-laboratory comparison exercise

The sets of results submitted by participants were assumed to be normally distributed and analysed statistically using Grubbs and Cochran's tests (Barwick *et al.,* 2001; Walker *et al.,* 2001) to detect outlying values. The Grubbs test was used to detect outlying values in the population of individual results and in the population of laboratory means, while Cochran's test was used to identify outlying values in the laboratory variances.

Using the certification of the total Pb concentration as an example, seven laboratories (1, 2, 3, 4, 5, 6, 7) submitted data for total Pb concentration. The Laboratory Means, standard deviation, and 95% confidence interval of the data from each laboratory are shown in Table 4.7 and Fig. 4.4a. The individual replicate results from each

laboratory were tested for outliers by using Grubbs 1, Grubbs 2, and Grubbs 3 tests. One replicate from Laboratory 7 (215) was identified as a Grubbs 1 outlier. The outlier was then removed, with the resulting outcome for Laboratory 7 shown in Fig. 4.4b. The Laboratory Means of data from each laboratory were then tested for possible Grubbs 1, Grubbs 2, Grubbs 3, and Cochran's outliers. No Grubbs outlier was identified but it was decided to reject the Laboratory Mean from Laboratory 4 as a Cochran's outlier (variance outlying), evaluation of the data at this stage being displayed in Fig. 4.4c. Although the Laboratory Mean from Laboratory 1 could perhaps have been rejected as a Cochran's outlier (variance outlying), it was decided to retain it as the spread of results from the six laboratories was considered acceptable. The data processing was therefore stopped at this stage, with a mean Pb concentration of 174 mg/kg. The data accepted on technical and statistical grounds for other total and acid-extractable elements are given in Figs 4.5 - 4.26.

Table 4.7 Raw data for the replicate results of total Pb concentration submitted by participants (expressed as concentration of element, mg/kg, corrected for moisture content), along with the calculated mean, standard deviation and 95% confidence interval.

Laboratory ID	Lab1	Lab2	Lab3	Lab4	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	172 171 178 168 166 186 185 194 184 183	172 172 168 177 176	169 168 168 171 174	150 144 146 163 167	164 163 164 160 161	174 181 172 177 173	182 180 192 191 215 189	
Laboratory Mean	179	173	170	154	162	175	191	172
SD	9	4	3	11	2	4	13	12
95% CI	6	5	3	13	2	5	13	11

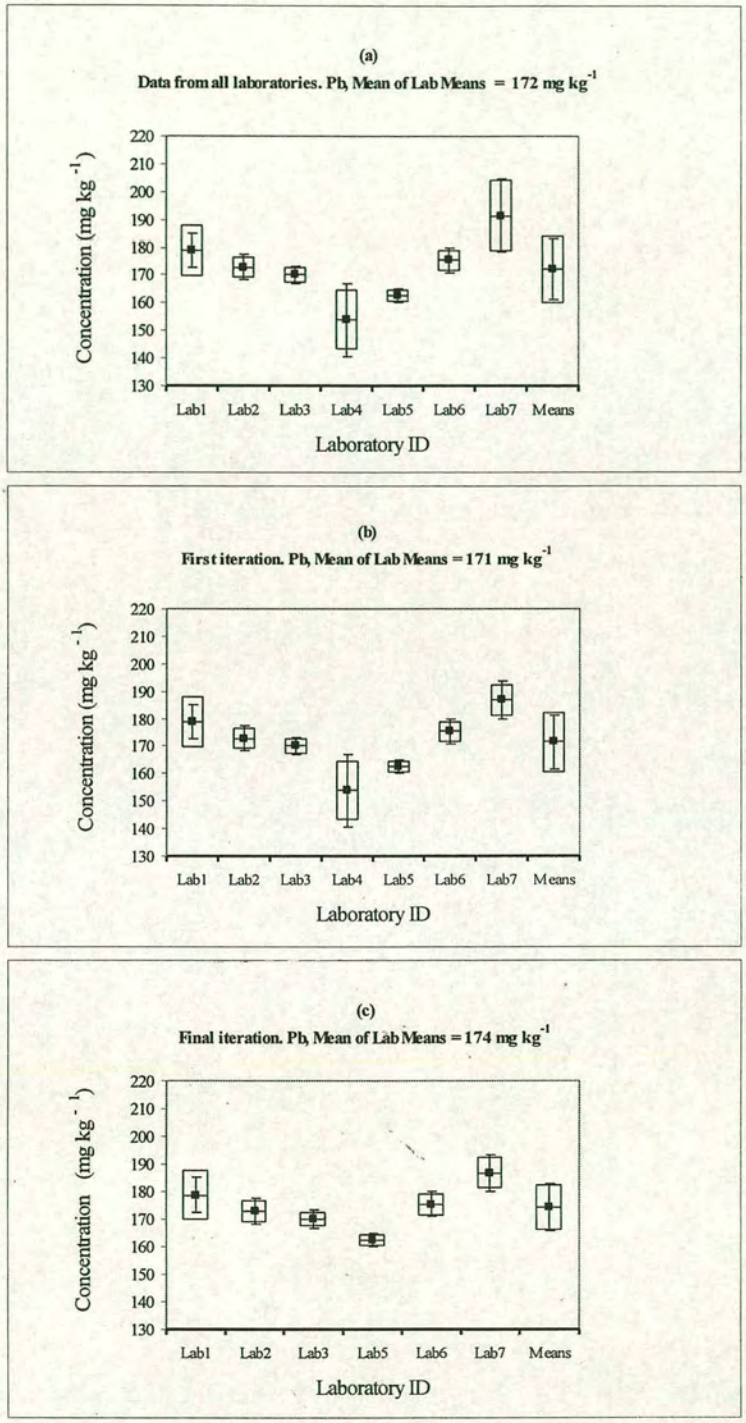


Figure 4.4 Inter-laboratory comparison results for total Pb concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

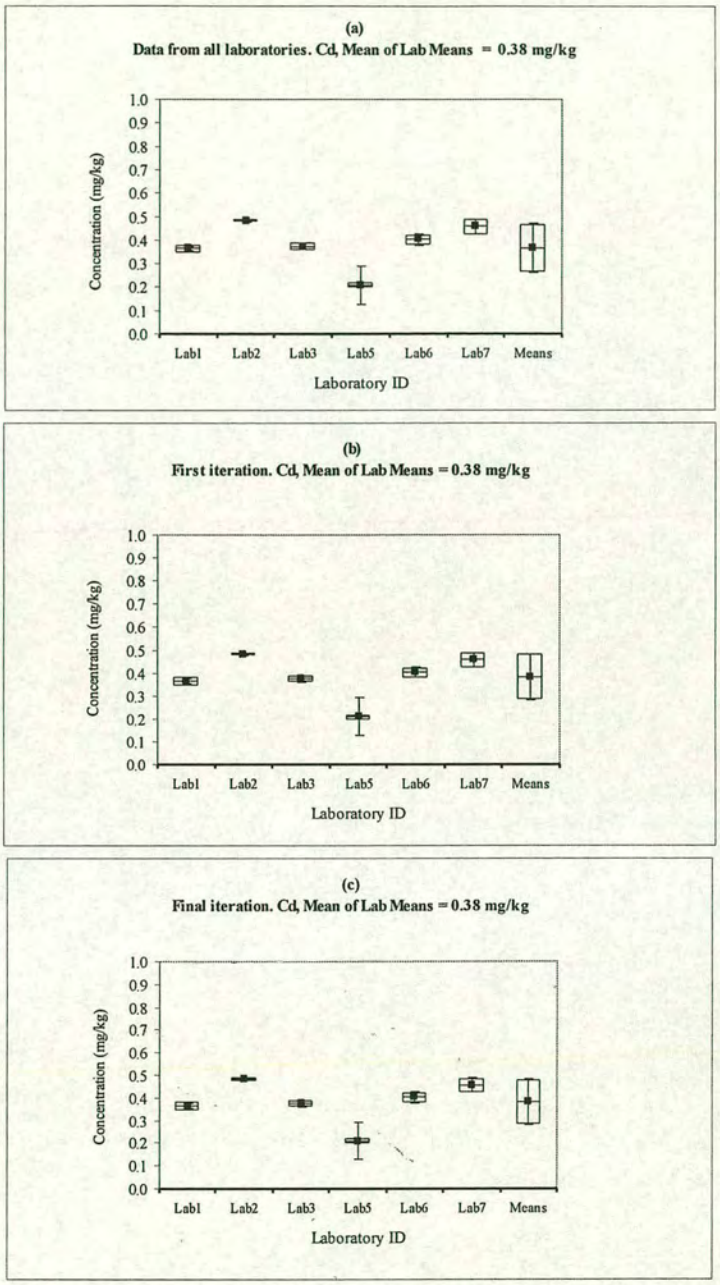


Figure 4.5 Inter-laboratory comparison results for total Cd concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

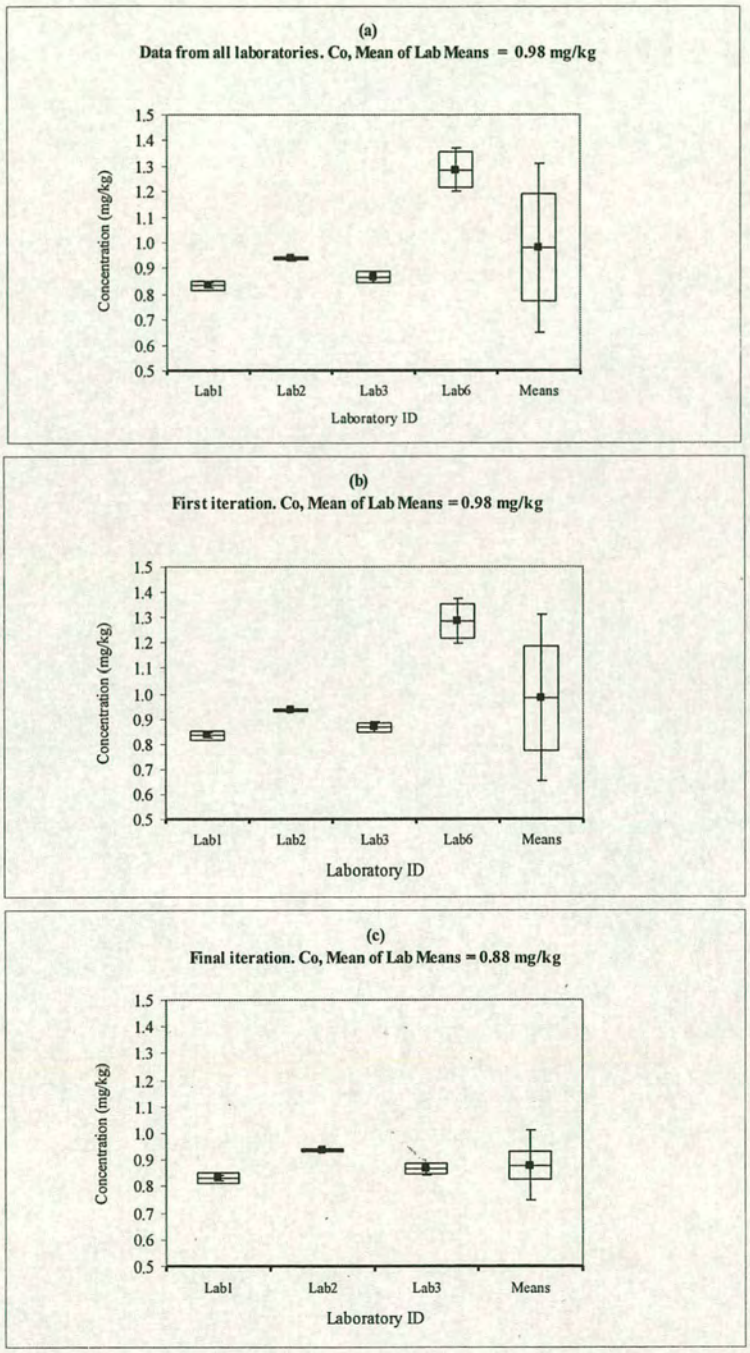


Figure 4.6 Inter-laboratory comparison results for total Co concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥⊤).

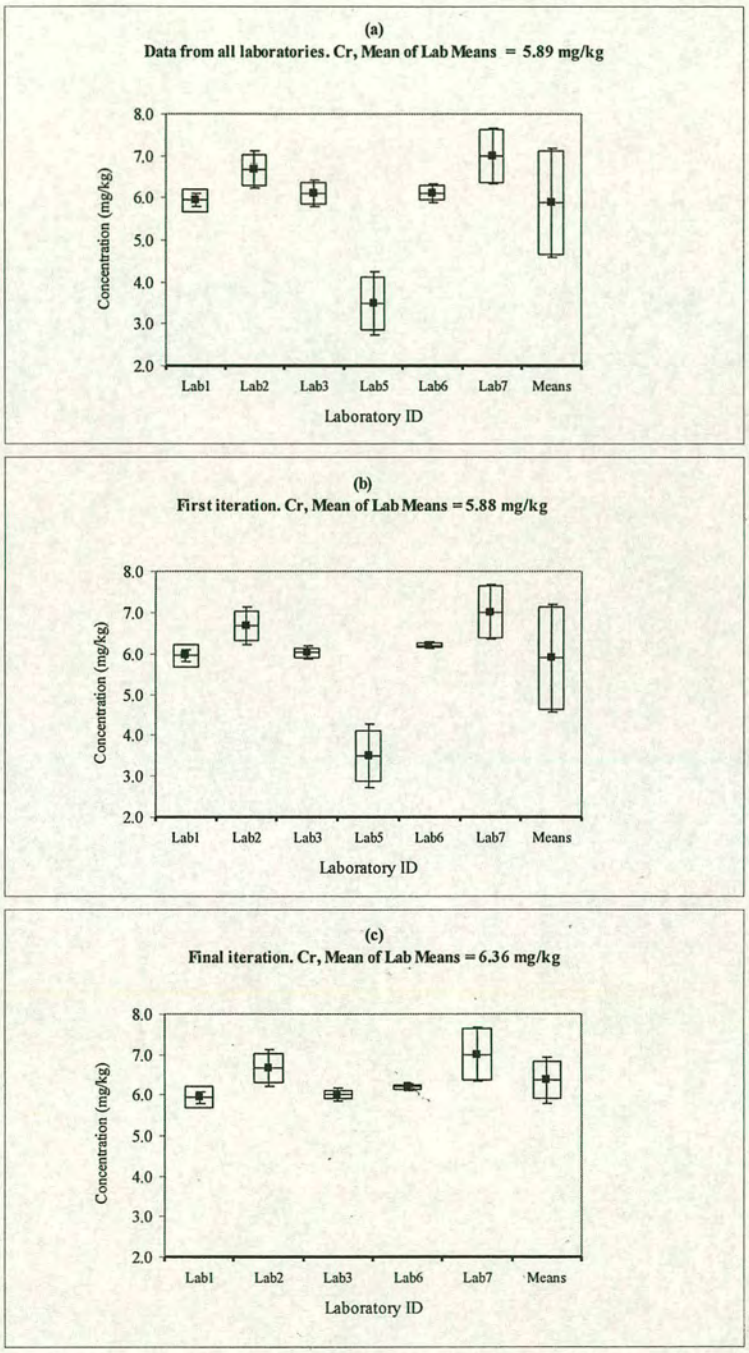


Figure 4.7 Inter-laboratory comparison results for total Cr concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

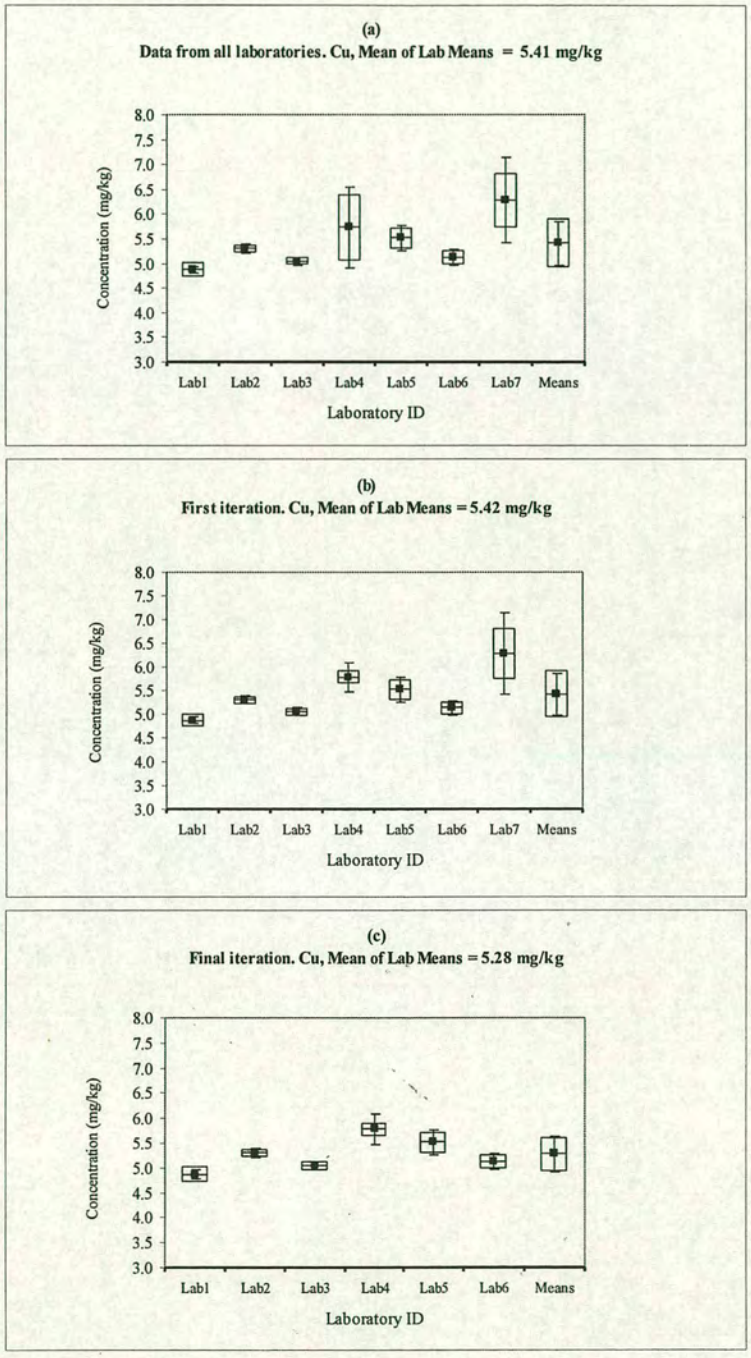


Figure 4.8 Inter-laboratory comparison results for total Cu concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

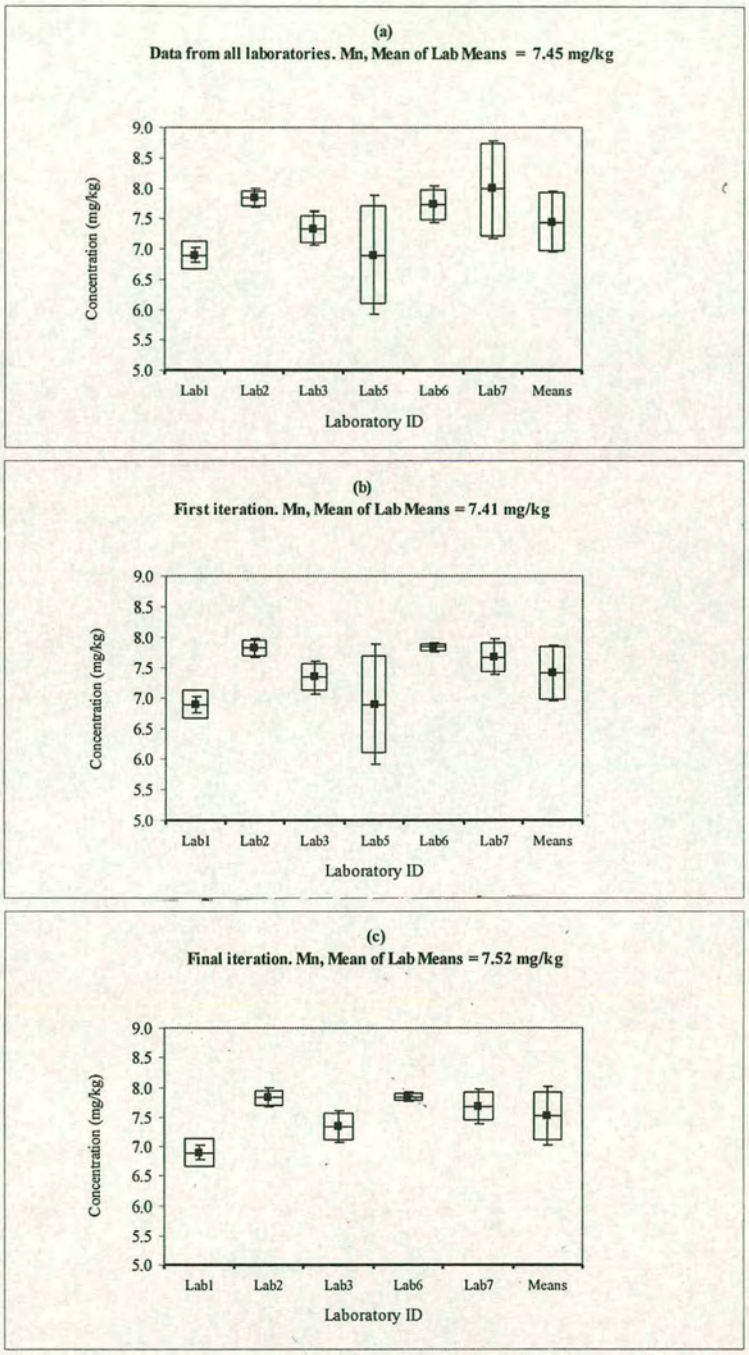


Figure 4.9 Inter-laboratory comparison results for total Mn concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥⊥).

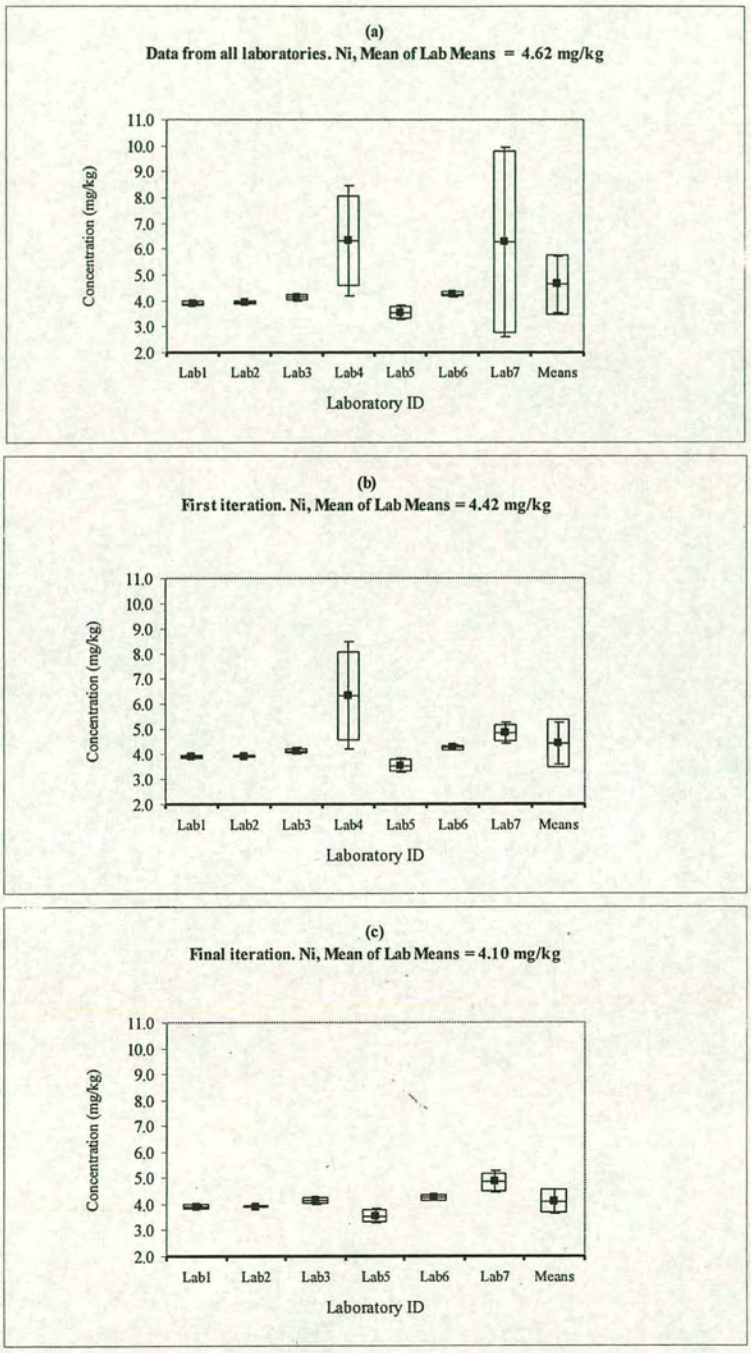


Figure 4.10 Inter-laboratory comparison results for total Ni concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥⊤).

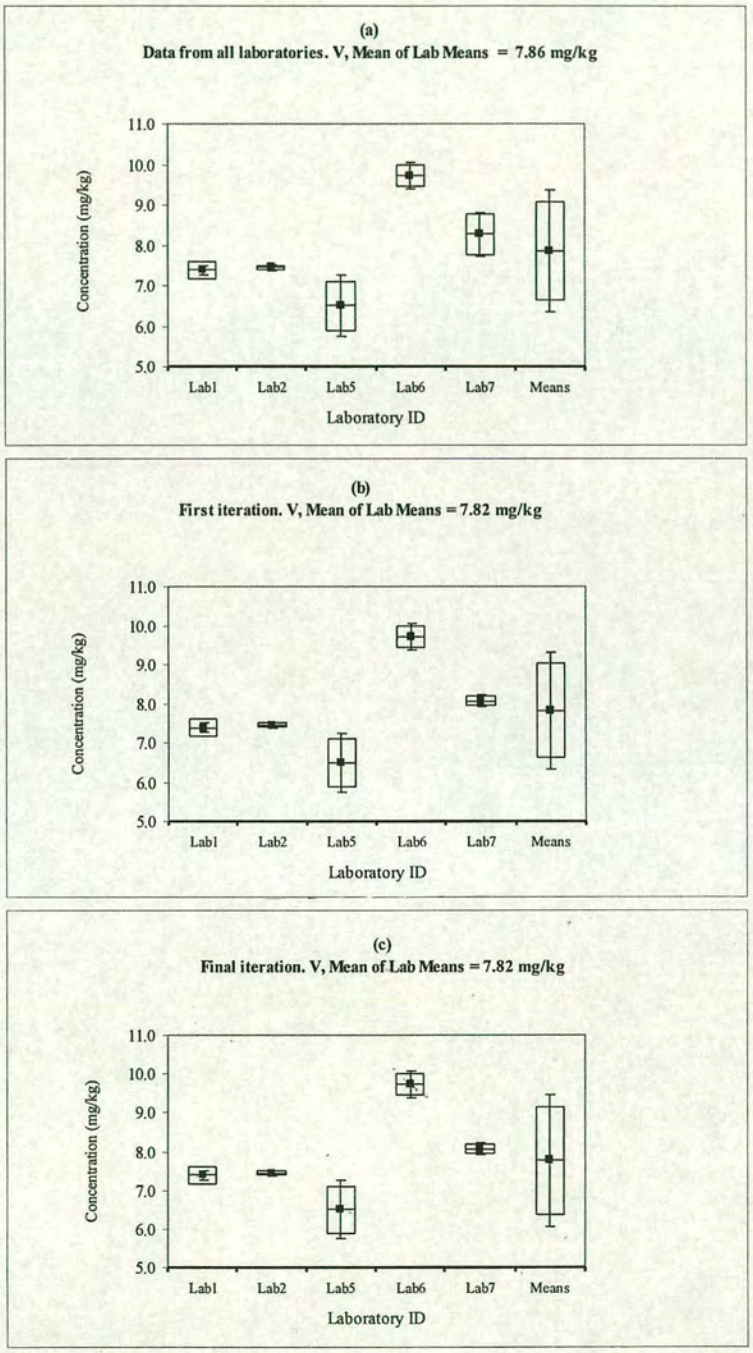


Figure 4.11 Inter-laboratory comparison results for total V concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

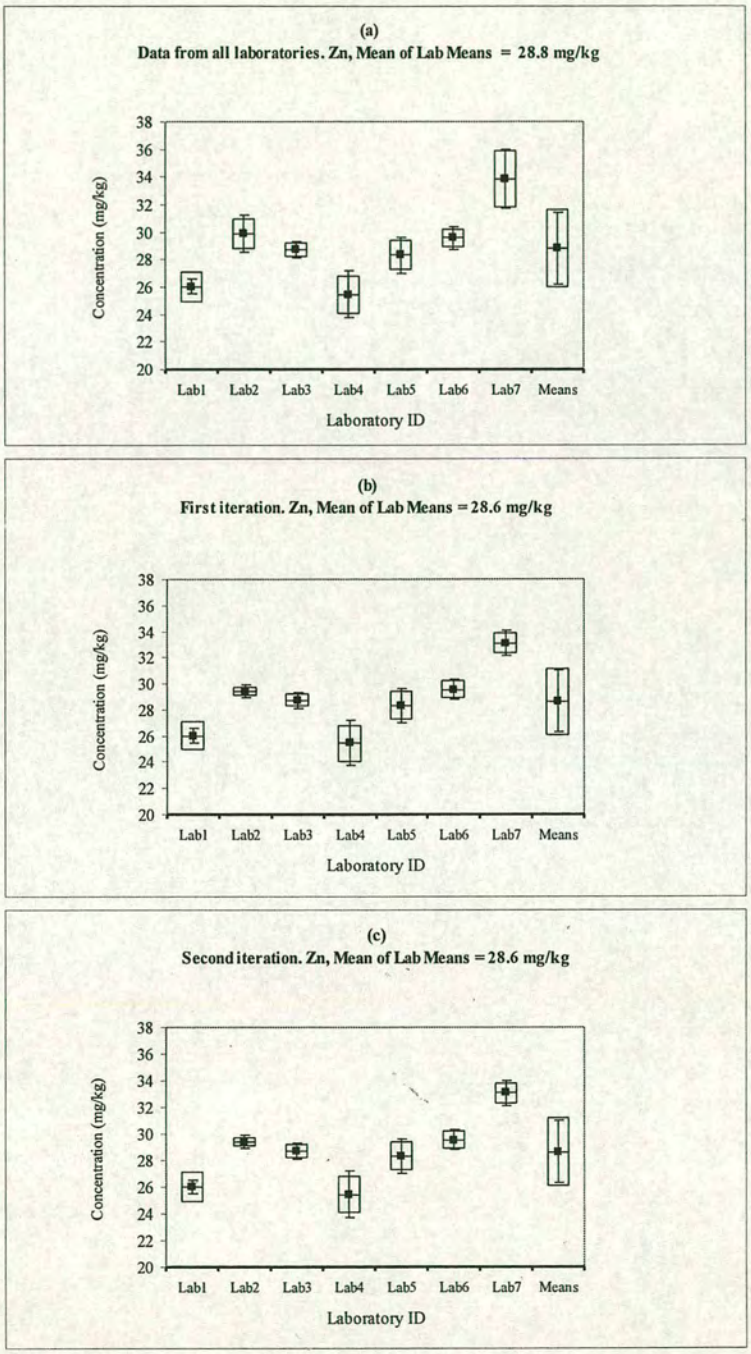


Figure 4.12 Inter-laboratory comparison results for total Zn concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥⊥).

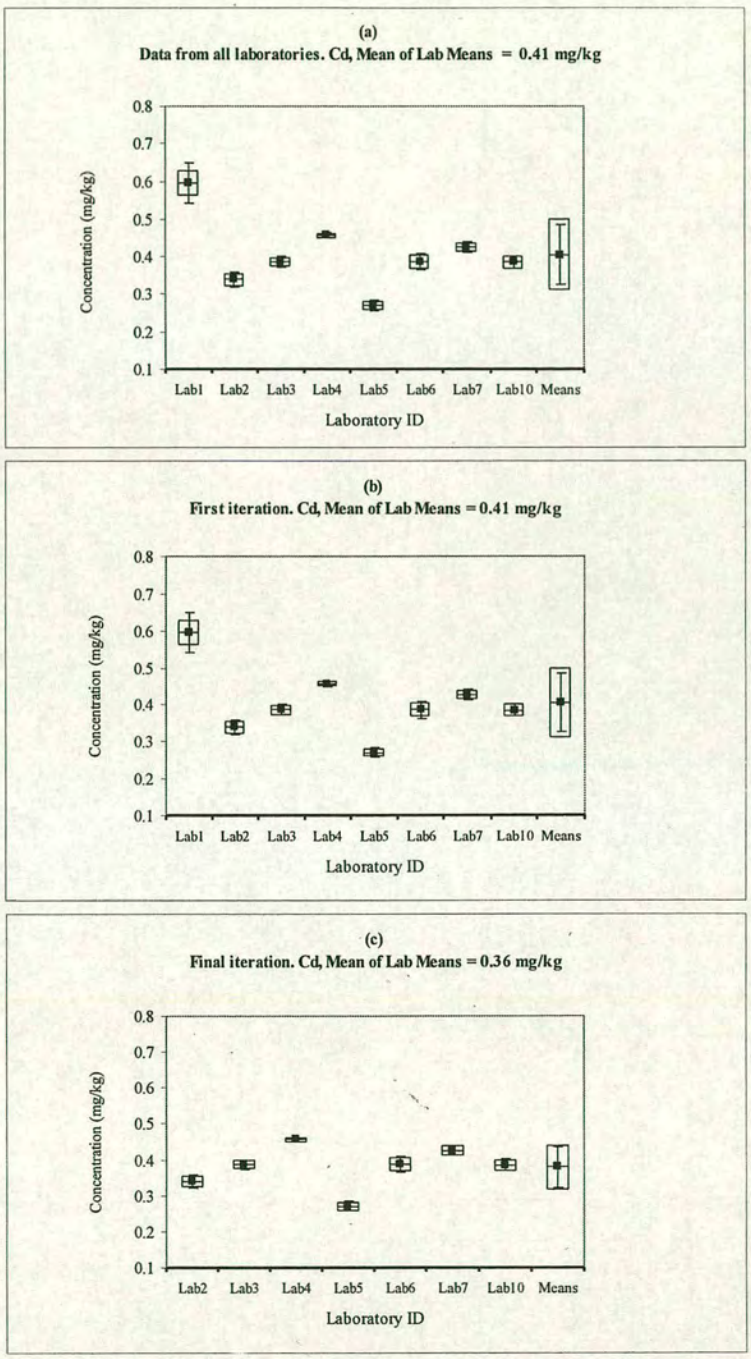


Figure 4.13 Inter-laboratory comparison results for acid-extractable Cd concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

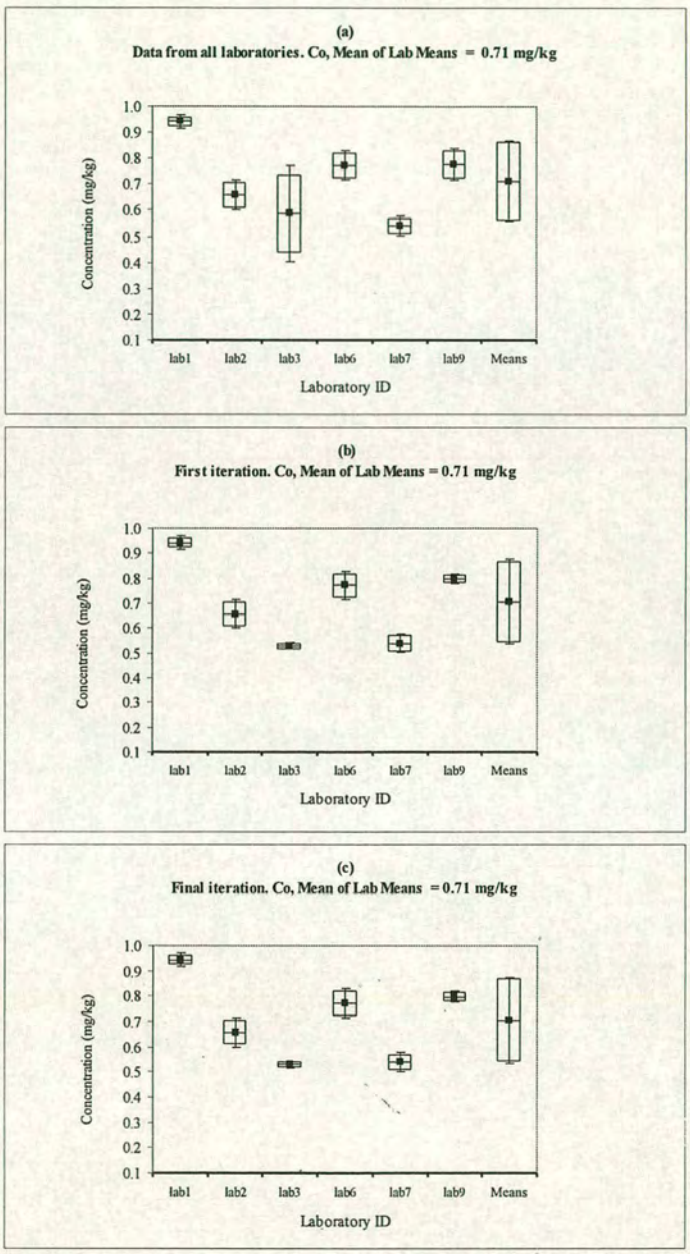


Figure 4.14 Inter-laboratory comparison results for acid-extractable Co concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

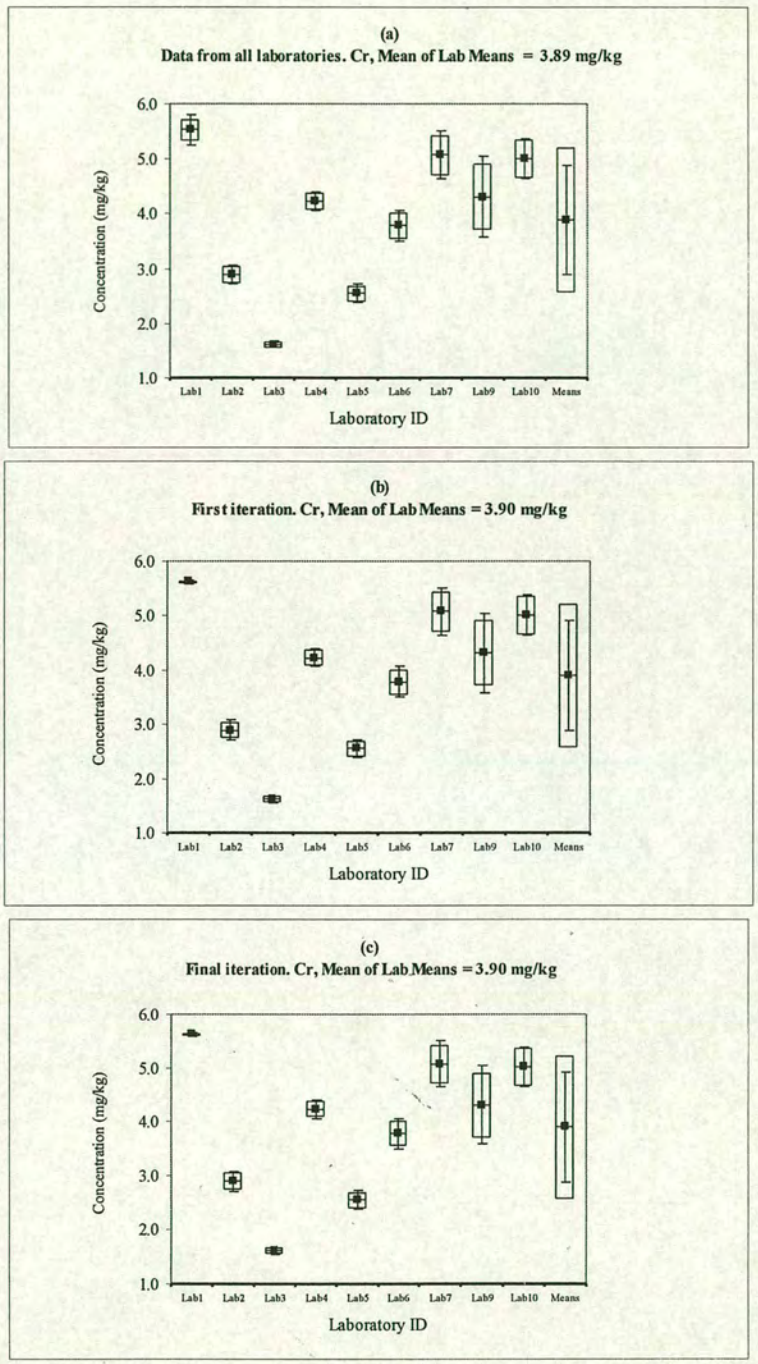


Figure 4.15 Inter-laboratory comparison results for acid-extractable Cr concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥⊤).

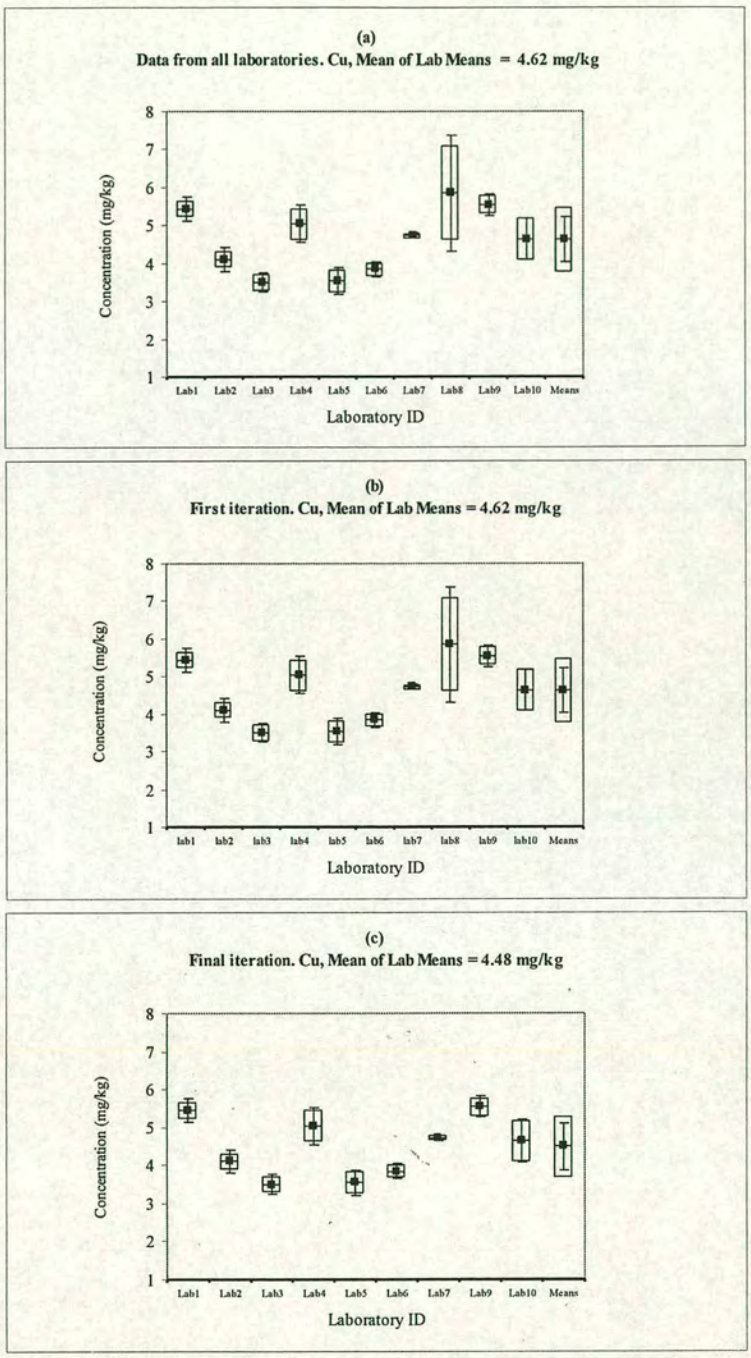


Figure 4.16 Inter-laboratory comparison results for acid-extractable Cu concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

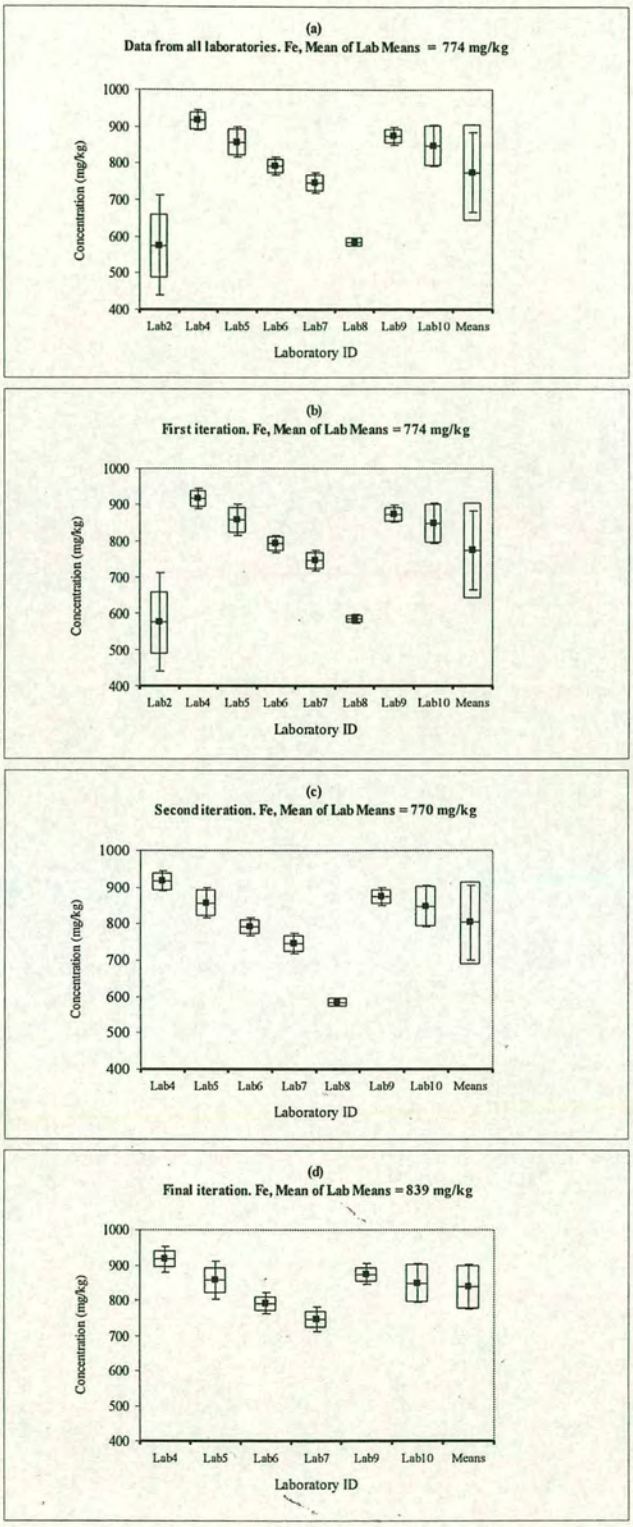


Figure 4.17 Inter-laboratory comparison results for acid-extractable Fe concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) second iteration, (d) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

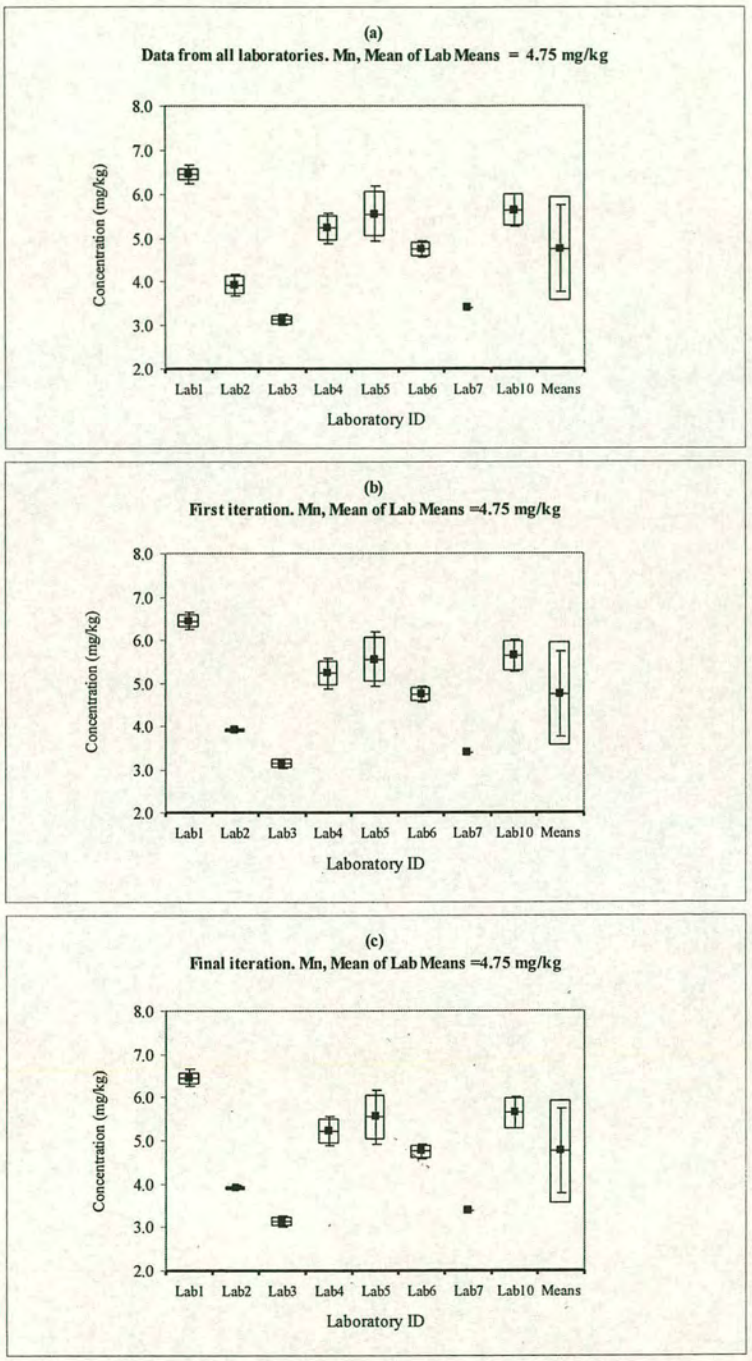


Figure 4.18 Inter-laboratory comparison results for acid-extractable Mn concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

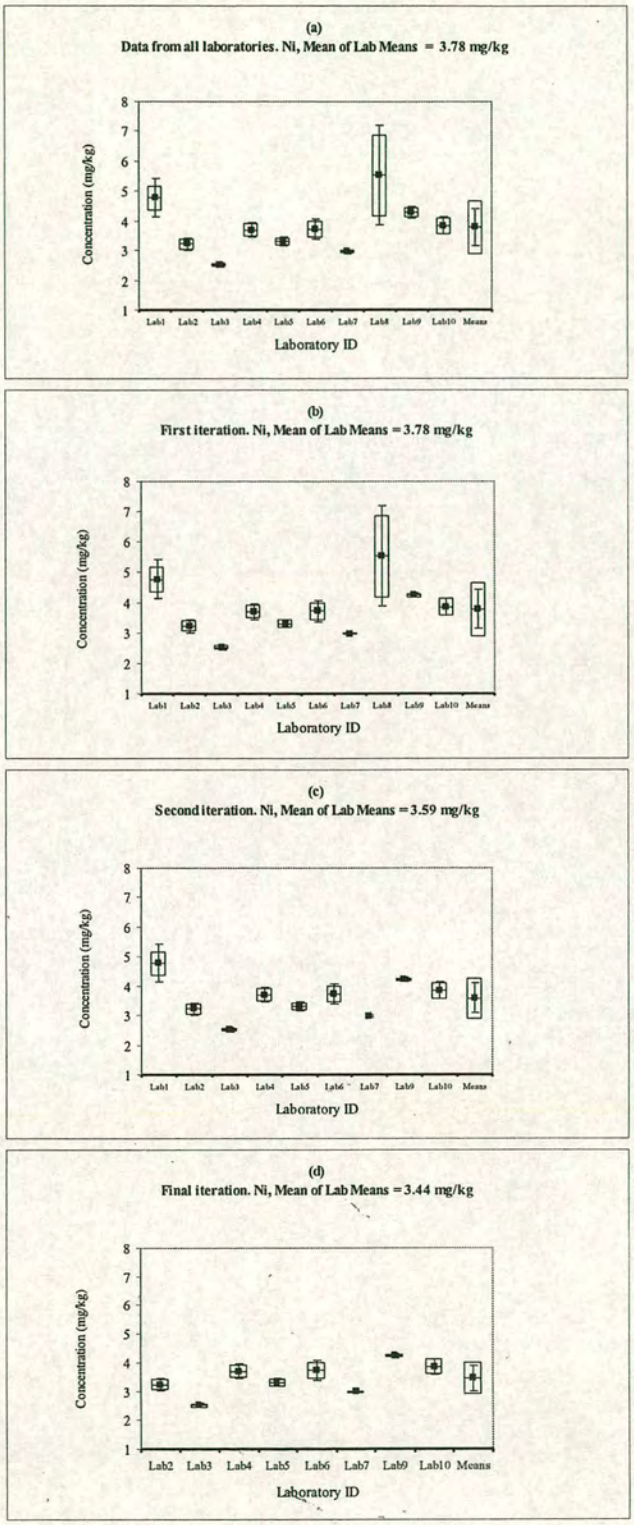


Figure 4.19 Inter-laboratory comparison results for acid-extractable Ni concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) second iteration, (d) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥⊥).

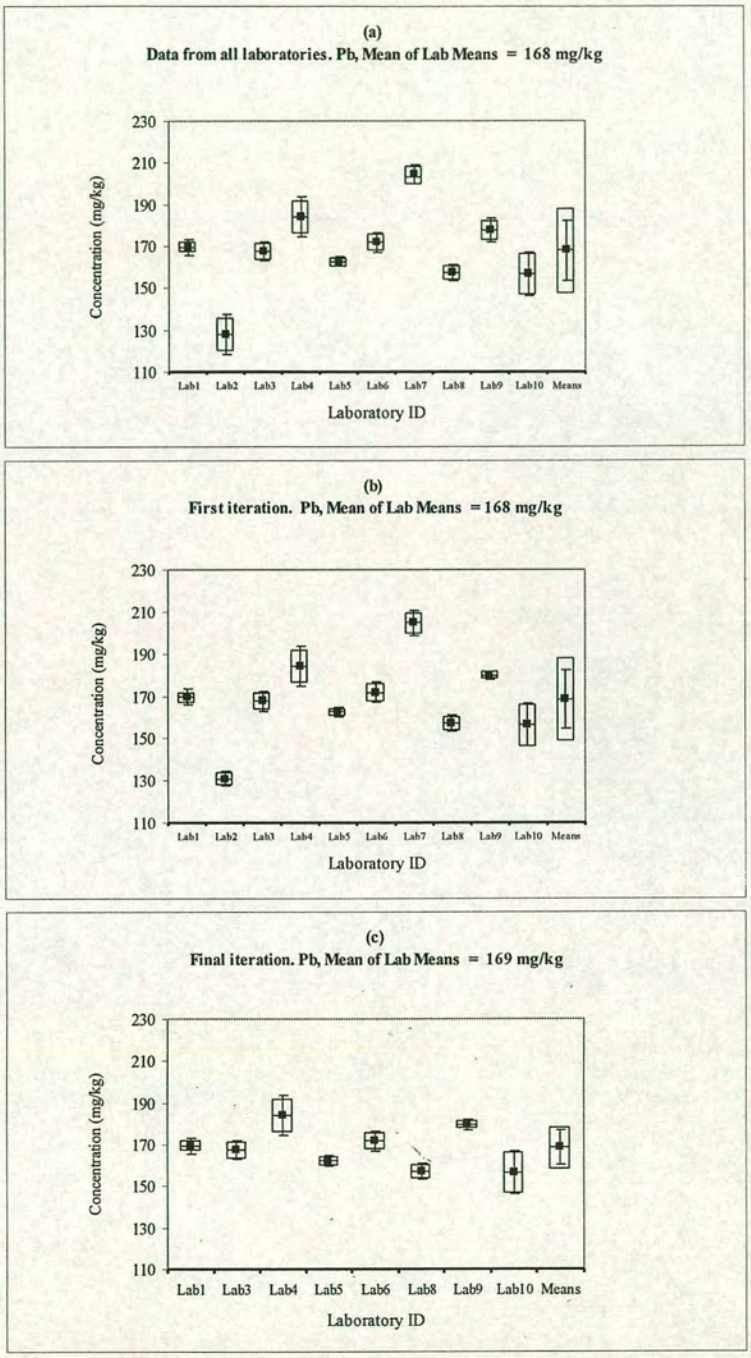


Figure 4.20 Inter-laboratory comparison results for acid-extractable Pb concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

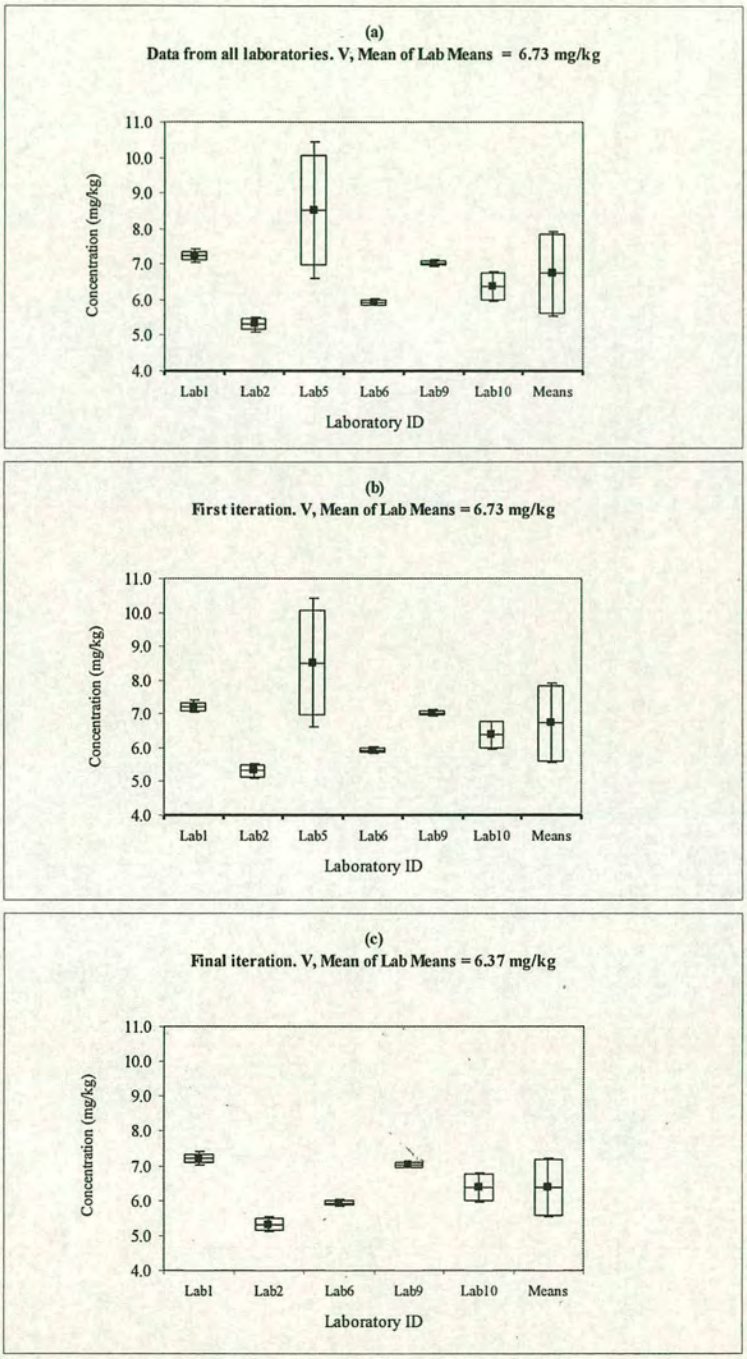


Figure 4.21 Inter-laboratory comparison results for acid-extractable V concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

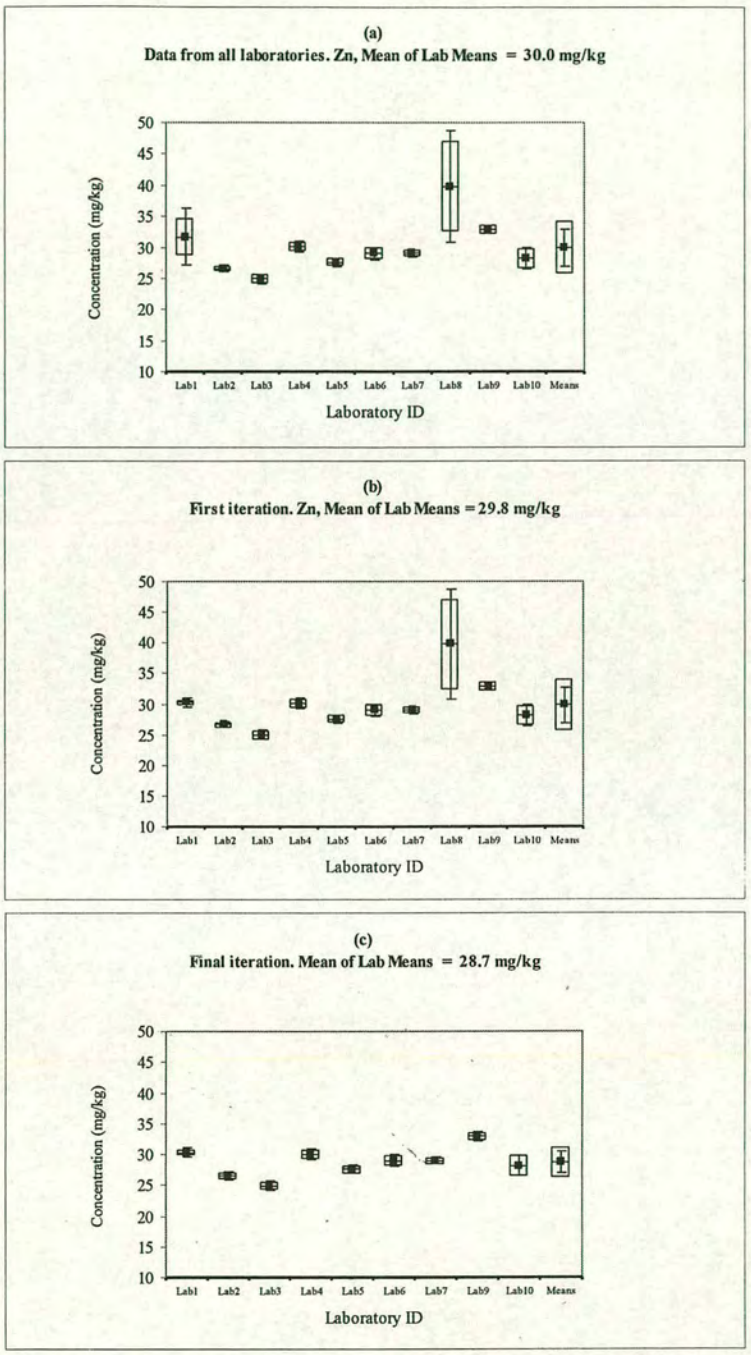


Figure 4.22 Inter-laboratory comparison results for acid-extractable Zn concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥⊤).

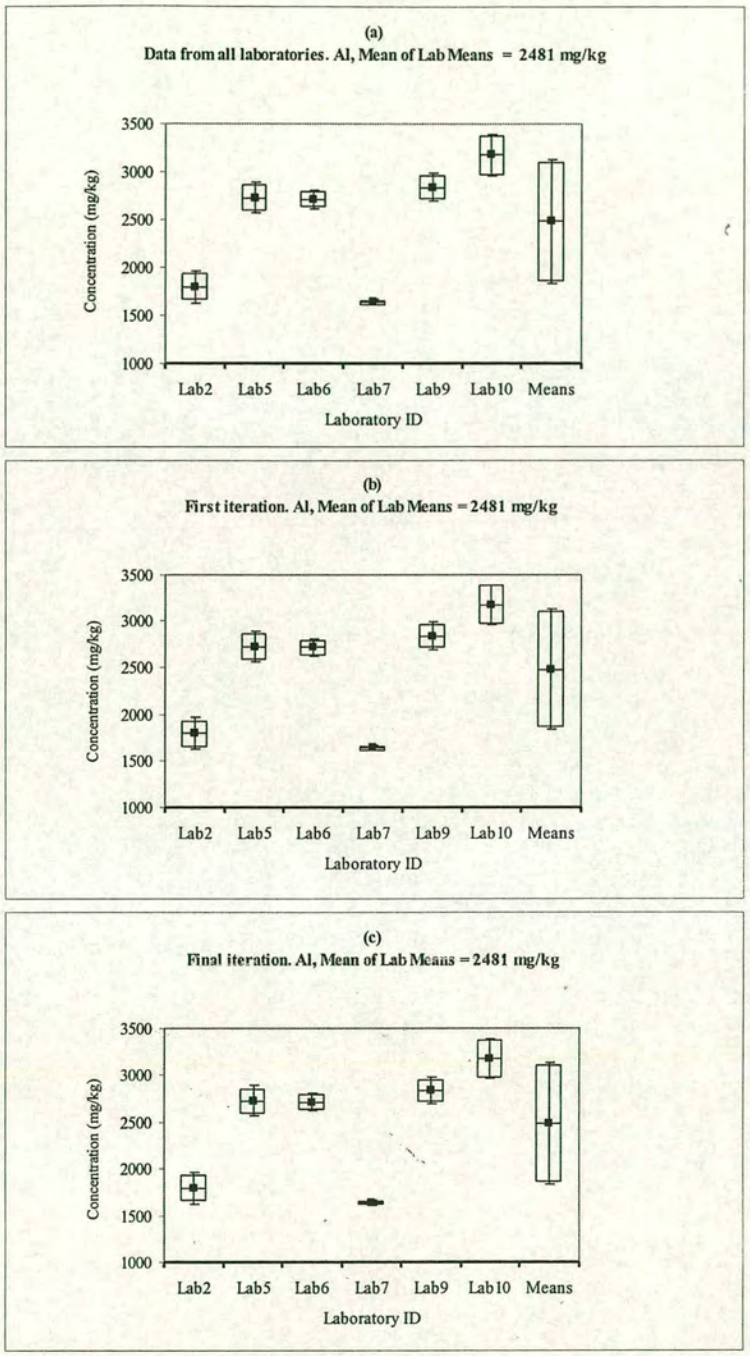


Figure 4.23 Inter-laboratory comparison results for acid-extractable Al concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

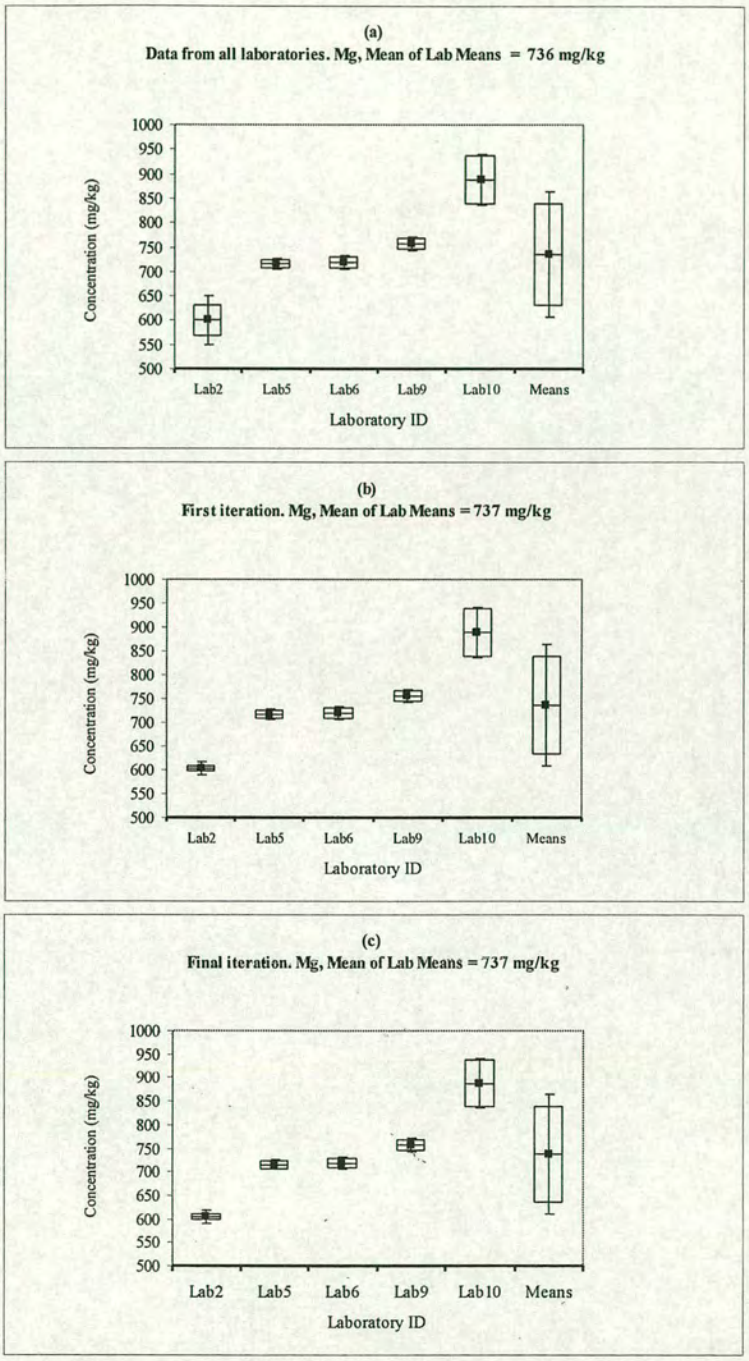


Figure 4.24 Inter-laboratory comparison results for acid-extractable Mg concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥).

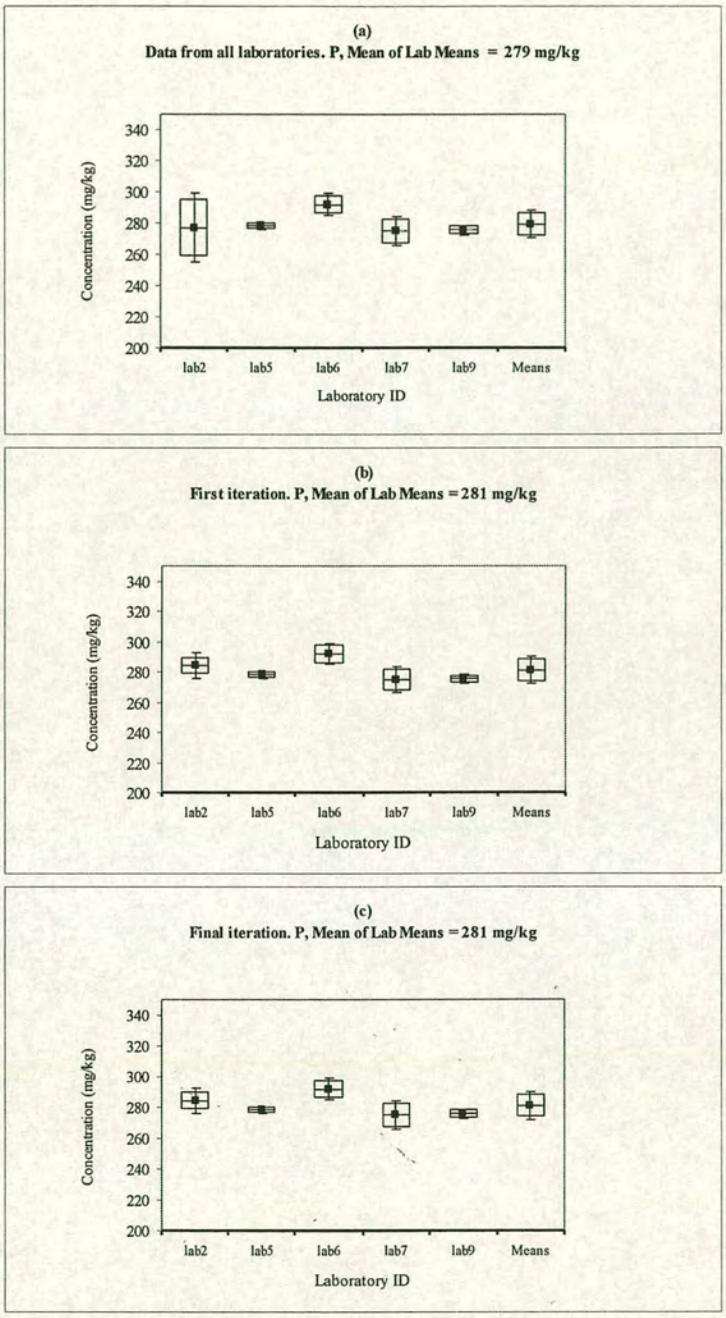


Figure 4.25 Inter-laboratory comparison results for acid-extractable P concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⌶).

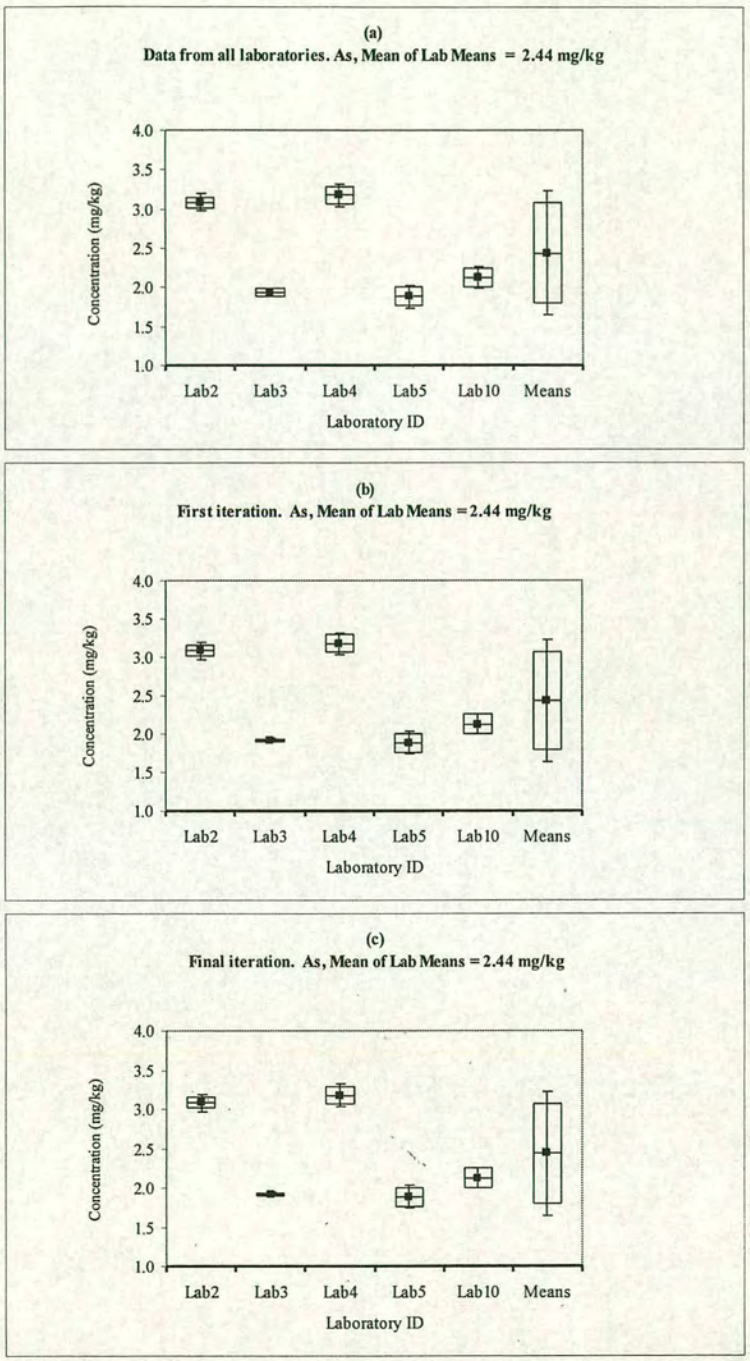


Figure 4.26 Inter-laboratory comparison results for acid-extractable As concentration (expressed as concentration, mg/kg, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥⊥).

4.5.3 Calculation of uncertainty

Uncertainty of measurement for the certified peat bog reference material was calculated according to the Guide on the Expression of Uncertainty in Measurement (GUM) and included uncertainties of characterisation, homogeneity and stability into the combined uncertainty. Estimation of uncertainties from characterisation and uncertainty of homogeneity were carried out according to the GUM. Uncertainty of stability was the most critical part. It must be monitored for a long period of study. For this reference material, uncertainty of the instability was not included in accordance with criteria for the production of a quality control reference material (Walker *et al.*, 2001).

Again using Pb as the example, the uncertainty of the value assigned to the total Pb concentration (174 mg/kg) of the ombrotrophic peat bog certified reference material was calculated according to a modification of the Guide on the Expression of Uncertainty in Measurement (GUM), using the equation:

$U_{CRM} = k\sqrt{u_{char}^2 + u_{bb}^2}$ where U_{CRM} = expanded uncertainty of the total Pb concentration of the peat bog certified reference material; k = coverage factor; u_{char} = uncertainty of the certified metal concentration in the ombrotrophic peat bog reference material; u_{bb} = uncertainty of the between-bottle inhomogeneity. The uncertainty of the instability (u_{stab}) was not included in view of the previously demonstrated stability and in accordance with criteria for the production of a quality control reference material.

As we do not have the full uncertainty budget from the participants in the inter-laboratory comparison exercise, u_{char} can be calculated from the equation:

$u_{char} = \frac{s}{\sqrt{l}}$ where s = standard deviation of laboratory means, i.e. 8 mg/kg; l = number of laboratories, i.e. 6. Therefore, u_{char} = 3.27 mg/kg, i.e. 1.88 % of 174.

The value of u_{bb} can be estimated from ANOVA of the data from homogeneity testing as: $u_{bb} = \sqrt{\frac{MS_{among} - MS_{within}}{n}}$ where MS_{among} = mean square among units, i.e. 38;

MS_{within} = mean square within units, i.e. 25; n = number of sub-samples per unit, i.e. 3. Therefore, u_{bb} = 2 mg/kg, i.e. 1.29 % of 174. Where MS_{among} component is lower than MS_{within}, u_{bb} was calculated from: $u_{bb} = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{\nu_{MS_{within}}}}$.

The expanded uncertainty of the value assigned to the total Pb concentration (174 mg/kg) in the ombrotrophic peat bog certified reference material can be calculated from:

$U_{CRM} = k \cdot u_c$ where $u_c = \sqrt{u_{char}^2 + u_{bb}^2}$, i.e. 2.28 %. Therefore, U_{CRM} (k =2) = 4.56 % of 174. Therefore the certified value for total Pb concentration in the ombrotrophic peat (low ash) reference material NIMT/UOE/FM/001 is 174 ± 8 mg/kg.

4.5.4 Certified and information-only values

By applying the same approach used for Pb to the other inter-laboratory comparison results, the certified values for total and acid-extractable concentrations (with a coverage factor of 2 for uncertainty) of elements determined in the ombrotrophic peat (low ash) reference material NIMT/UOE/FM/001 were calculated and displayed in Table 4.8 and Table 4.9, respectively. The corresponding certificates were issued (Appendix F). Where concentration data were not sufficient and considered too variable, the arithmetic means (± 1 S.D.) are given as information-only values for some elements. The full list of certified (coverage factor of 2) and information-only (± 1 S.D.) values is displayed in Table 4.10.

The acid-extractable concentrations of Cd, Pb, and Zn are similar to their corresponding total concentrations (Table 4.10), whereas the acid-extractable concentration of Cr and of some major elements such as Al, Na, and Ti are clearly lower than their corresponding total concentrations. This suggests that Cr and these major elements occur in matrices that cannot be dissolved by conventional acid digestion methods. The employment of HF for wet digestion is needed in the study of Cr and some major elements. The variation of the acid-extractable results for some elements such as Al is probably a consequence of the range of digestion methods used by the participants.

In addition to elemental concentration data, information on Pb isotopic composition was provided by three laboratories. Reported mean values of 1.1766 ± 0.0008, 1.1759 ± 0.0006, and 1.1765 ± 0.0003 yielded an overall information-only value of 1.1763 ± 0.0004 (± 1 SD) for the $^{206}Pb/^{207}Pb$ ratio.

Table 4.8 Mean of Laboratory Means, standard deviation, combined and individual uncertainty calculation for total elemental concentrations in the ombrotrophic peat (low ash) reference material NIMT/UOE/FM/001.

Element	Mean of Laboratory Mean	$u_{char} = s/\sqrt{l}$			u_{bb} [%]	U_{CRM} (k=2) [%]	Certified value ± U (k=2) [mg/kg]
		S [mg/kg]	l	u_{char} [%]			
Cd	0.38	0.10	6	10.74	1.34	21.65	0.38 ± 0.08
Co	0.88	0.05	3	3.28	3.86	10.14	0.88 ± 0.09
Cr	6.36	0.46	5	3.23	1.25	6.94	6.36 ± 0.44
Cu	5.28	0.33	6	2.55	9.54	19.76	5.28 ± 1.04
Mn	7.52	0.40	5	2.38	1.34	5.46	7.52 ± 0.41
Ni	4.10	0.43	6	4.28	1.34	8.97	4.10 ± 0.37
V	7.82	1.20	5	6.86	0.49	13.76	7.82 ± 1.08
Zn	28.6	2.5	7	3.30	0.41	6.66	28.6 ± 1.9

Table 4.9 Mean of Laboratory Means, standard deviation, combined and individual uncertainty calculation for acid-extractable elemental concentrations in the ombrotrophic peat (low ash) reference material NIMT/UOE/FM/001.

Element	Mean of Laboratory Mean	$u_{char} = s/\sqrt{l}$			u_{bb} [%]	U_{CRM} (k=2) [%]	Certified value ± U (k=2) [mg/kg]
		S [mg/kg]	l	u_{char} [%]			
Cd	0.36	0.06	7	6.30	1.34	12.88	0.36 ± 0.05
Co	0.71	0.16	6	9.20	2.38	19.01	0.71 ± 0.13
Cr	3.90	0.44	9	11.28	2.31	23.03	3.90 ± 0.90
Cu	4.48	0.78	9	5.80	5.72	16.29	4.48 ± 0.73
Fe	839	25	6	2.97	1.24	6.44	839 ± 54
Mn	4.74	1.18	8	8.78	2.50	18.26	4.74 ± 0.87
Ni	3.44	0.55	8	5.65	1.34	11.62	3.44 ± 0.40
Pb	169	10	8	2.09	0.98	4.62	169 ± 8
V	6.37	0.79	5	5.55	1.45	11.46	6.37 ± 0.73
Zn	28.7	2.3	9	2.67	0.98	5.69	28.7 ± 1.6
As	2.44	0.64	5	11.73	1.34	23.61	2.44 ± 0.58
Al	2481	618	6	10.17	1.94	20.70	2481 ± 514
Mg	737	102	5	6.19	1.73	12.86	737 ± 95
P	281	7	5	1.11	0.55	2.48	281 ± 7

Table 4.10 Certified values with uncertainties (coverage factor of 2) and information-only (italics) values [± 1 SD (n ≤ 4)] for the elemental concentration of the ombrotrophic peat (low ash) reference material NIMT/UOE/FM/001.

Element (x, y)	Certified values (mg kg^{-1})	
	Total concentration	Acid-extractable concentration
Cd (6, 8)	0.38 ± 0.08 (6)	0.36 ± 0.05 (7)
Co (4, 6)	0.88 ± 0.09 (3)	0.71 ± 0.13 (6)
Cr (6, 9)	6.36 ± 0.44 (5)	3.90 ± 0.90 (9)
Cu (7, 10)	5.28 ± 1.04 (6)	4.48 ± 0.73 (9)
Fe (4, 8)	*921 ± 84 (4)*	839 ± 54 (6)
Mn (6, 8)	7.52 ± 0.41 (5)	4.74 ± 0.87 (8)
Ni (7, 10)	4.10 ± 0.37 (6)	3.44 ± 0.40 (8)
Pb (7, 10)	174 ± 8 (6)	169 ± 8 (8)
V (5, 6)	7.82 ± 1.08 (5)	6.37 ± 0.73 (5)
Zn (7, 10)	28.6 ± 1.9 (7)	28.7 ± 1.6 (9)
As (4, 5)	*2.44 ± 0.55 (3)*	2.44 ± 0.58 (5)
Hg (2, 2)	*0.169 ± 0.007 (2)*	*0.164 ± 0.020 (2)*
Al (3, 6)	*3692 ± 347 (3)*	2481 ± 514 (6)
Ca (3, 4)	*683 ± 198 (3)*	*763 ± 172 (4)*
Mg (2, 5)	*582 ± 168 (2)*	737 ± 95 (5)
Na (3, 3)	*817 ± 307 (3)*	*229 ± 78 (3)*
P (2, 5)	*265 ± 8 (2)*	281 ± 7 (5)
Ti (3, 3)	*357 ± 18 (3)*	*110 ± 11(3)*

x and y indicate the number of laboratories that submitted results for total and acid-extractable elemental concentrations, respectively.
Under total and acid-extractable concentration, the number in brackets indicates the number of accepted laboratory results used in the certification exercise for each element.

Chapter 5
The Application of Isotope Dilution Mass Spectrometry (IDMS) to the Determination of Pb in Peat

5.1 Isotope dilution mass spectrometry (IDMS)

Isotope dilution mass spectrometry (IDMS) is based on the addition of a known amount of an enriched isotope ("spike") of the element to be determined to a sample. After equilibration of the natural isotopes in the sample with the spike isotopes, mass spectrometry is used to measure the altered isotopic ratio(s). This change enables the concentration of the element to be determined very accurately and precisely. A major advantage of the technique is that chemical separations need not be quantitative. Recently, IDMS has been recognised by the Comité Consultatif pour la Quantité de Matière (CCQM) as a primary method of measurement (Prohaska *et al.,* 2000). The CCQM has defined a definite method or primary method of measurement as a method which is completely described and understood, having the highest metrological qualities and for which the results can be given with a complete uncertainty statement.

The IDMS procedure as applied to Pb is outlined in Figure 5.1. The technique is based on primary standards, the process of weighing, and the mass spectrometric isotope ratio measurement. Thus, the weighing process links the technique to the fundamental SI unit, the kilogram. The mass spectrometric isotope ratio measurement process ties the technique to the relative atomic masses of the elements, linking mass to the amount of substance and thus to the mole, the fundamental unit of chemistry (Watters *et al.*, 1997). The direct link between amount of an element in an unknown sample and a primary chemical standard is shown in Figure 5.1. The accurately known chemical purity of the primary assay standard is used to obtain an accurate concentration for the "spike" solution by isotope ratio measurement of a mixture of these two solutions. This procedure is called "spike calibration". The process of quantitatively diluting the enriched ^{206}Pb atom fraction in the spike solution with the isotopic natural assay standard is often referred to as "reverse isotope dilution". The spike calibration is an important and integral part of the isotope dilution process through the spike to the primary assay standard. The

isotope dilution analysis requires accurate measurement of isotope ratios of two mixtures, spike : unknown, and spike : assay standard. If the conditions of ratio measurement are consistent between the spike calibration and the sample measurement, and assuming accurate weighing, potential systematic errors in the measurement processes are cancelled or minimised in the final result.

For IDMS determination of Pb using ICP-MS, the ratio measurement relative standard deviation can be controlled to 0.2 %. It follows that all sample preparation procedures must be more precise than the experimental ratio measurement in order to achieve the limiting precision for the whole analysis. Gravimetric procedures for solution sampling are inherently more precise and accurate, and were utilised in this procedure.

The best use of IDMS requires an optimum mixture of the spike and sample. In theory the best measurement situation occurs when the isotope ratio of the mixture equals the square root of the product of the isotope ratios of the spike and the natural isotope. In practice, other factors must be considered. For example, the best mass spectrometric precision is achieved for ratios near one. Ion counting uncertainty, background corrections, and the relatively limited dynamic range of the ICP-MS with respect to ratio measurement must also be considered. A reasonable rule of thumb is to mix the spike and the sample solution on an equimolar basis.

Equimolar mixing of the spike and sample will result in an isotope ratio of between 1/4 and 4/1 for most elements, assuming the spike is a highly enriched isotope (>90% enriched) and the major natural isotope is at least 50%. For lead, this 1 : 1 rule of thumb is adequate (92% enriched ^{206}Pb, and the major natural isotope ^{208}Pb is 52.4% abundant) The isotopic information for Pb is displayed in Tables 5.1a and 5.1b.

This chapter can be divided into two major parts; first the IDMS was carried out on a digested sample (peat reference material) solution, while the same analytical procedure was applied to the solid peat reference material in the second part.

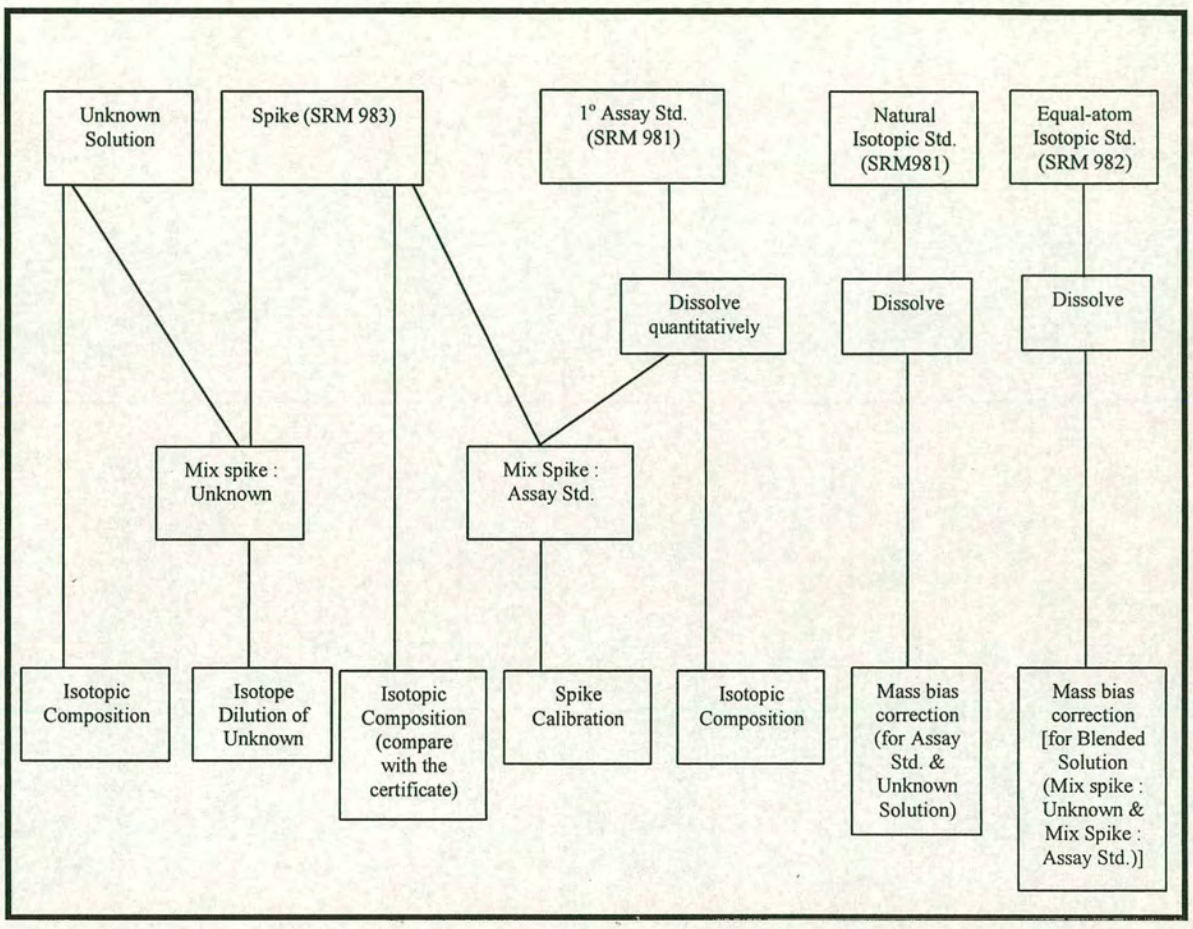


Figure 5.1 Scheme for the application of IDMS to the determination of Pb in an unknown solution.

Table 5.1a Isotopic information for Pb in three NIST standard reference materials SRM 981, SRM 982, and SRM 983.

SRM 981 (Natural Isotopic Standard)		SRM 982 (Equal-atom Isotopic Standard)		SRM 983 (^{206}Pb enriched spike solution)	
Isotope	%Abundance	Isotope	%Abundance	Isotope	%Abundance
204	1.4255	204	1.0912	204	0.0342
206	24.1442	206	40.0890	206	92.1497
207	22.0833	207	18.7244	207	6.5611
208	52.3470	208	40.0950	208	1.2550

Table 5.1b Certified isotopic ratios of Pb in three NIST standard reference materials SRM 981, SRM 982, and SRM 983.

Isotope ratios	Certified Isotope Ratios		
	SRM 981	SRM 982	SRM 983
204/206	0.059042 ± 0.000037	0.027219 ± 0.000027	0.000371 ± 0.000020
207/206	0.91464 ± 0.00033	0.46707 ± 0.00020	0.071201 ± 0.000040
208/206	2.1681 ± 0.0008	1.00016 ± 0.00036	0.013619 ± 0.000024

5.2 Application of IDMS to the determination of Pb in the digested sample solution (peat reference material)

5.2.1 Sample preparation

5.2.1.1 Preparation of unknown sample solution

The ombrotrophic peat reference material NIMT/UOE/FM/001 was digested according to the adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat. The concentration of Pb in the digest solution was measured at ~1.5 mg/l by ICP-OES. This value is used in further calculation.

5.2.1.2 Preparation of ^{206}Pb enriched spike solution (SRM 983)

The spike solution was prepared to have a nominal concentration of ~1.5 mg/l. The 208/206 ratio was to be measured to confirm the identity and integrity of the spike. However, the certified values (Table 5.1b) will be used in the calculation.

The ~ 0.1 g piece of Pb metal (SRM 983) (99.9 % purity, *w*) (*m1*) was accurately weighed to ±0.1 mg. Then the piece of metal was dissolved in 10 ml of 1 : 3 w/w HNO_3 : H_2O on gentle heating. The solution was diluted in 2% v/v HNO_3 to a total mass of 100 g (*d1*). This solution was further diluted by accurately weighing 0.1 g solution (*m2*) to ±0.1 mg and then diluting in 2% (v/v) HNO_3 to a total mass of 100 g (*d2*). The Pb concentration of the spike solution was calculated from $c_{spike} = (m1.m2.w)/(d1.d2.M)$, where *M* is the relative atomic mass of Pb in SRM 983. The weights used in the associated calculation are shown below:

c_{spike} = $(m1.m2.w)/(d1.d2.M)$

= [(0.1113 g)(0.1854 g)(0.999)]/[(101.1951 g)(100.7041 g)(206.06 g/mol)]

= 9.744×10^{-9} mol/g

= 0.009744 µmol/g

5.2.1.3 Preparation of assay standard solution

A primary assay standard was provided in the form of Pb metal having high chemical purity (*w*) (99.9 %) and nominal natural isotopic composition. This material was used to calibrate the spike by "reverse isotope dilution". The most accurate results are achieved

in isotope dilution analysis when the spike is calibrated, and the unknown samples are analysed at the same time. In this experiment SRM 981 was used as assay standard. This solution was prepared by diluting the 1272 mg/l SRM 981 standard solution which had been prepared by another analyst in the laboratory. The 1272 mg/l standard was prepared by dissolving a 1.272 g piece of Pb metal SRM 981 (*m1*) in 1 : 3 w/w HNO_3 : H_2O on gentle heating. The solution was then diluted in 2% v/v HNO_3 to a total mass of 1000 g (*d1*). This solution was named Assay1. A more dilute solution was needed, so an accurately weighed 0.1 g of Assay1 solution (*m2*) to ±0.1 mg was then diluted in 2% (v/v) HNO_3 to a total mass of 100 g (*d2*). This solution was named Assay2. The concentration of Pb in Assay2 (c_z) was calculated according to the equation: $c_z = (m1.m2.w)/(d1.d2.M)$, where M is the relative atomic mass of Pb in SRM 981 (207.22).

5.2.1.4 Preparation of spike : unknown sample solution mixtures

Four spike : unknown replicate sample solution mixtures were prepared as follows. A 1 g aliquot of sample was weighed, to an accuracy of ±0.1 mg, into a suitable container. To each sample aliquot was added a spike from the spike solution. The spike solution had been prepared to provide a concentration similar to that of the unknown solution, to enable approximately 1 : 1 mixing. The spike solution added to each sample aliquot had been carefully weighed using the same procedure as for the unknown sample solution.

5.2.1.5 Preparation of spike : assay standard mixtures

At the same time as the spike : unknown sample mixtures were prepared, four 1 g aliquots of the spike solution were weighed into clean beakers so that Pb concentration could be determined in the "spike calibration". Two of these aliquots were weighed out before spiking the unknown samples and two after the unknown samples had been spiked. This process verified the integrity of the spike throughout the entire spiking procedure. The spike calibration is achieved by a "reverse isotope dilution" experiment against the two natural Pb solutions prepared from the assay standard.

The four spike : assay standard mixtures were named SpikeCal1, SpikeCal2, SpikeCal3, and SpikeCal4. The spike solutions in SpikeCal1 and SpikeCal2 were weighed out before

the unknown samples had been spiked, while those for SpikeCal3 and SpikeCal4 were weighed out afterwards. The mixtures were prepared by 1 : 1 mixing of the spike solution and the assay standard solution.

5.2.1.6 Blanks

Since only high purity reagents were used, which (for the blank) would lead to extreme ratios in the mixtures and consequent poor reliability for the enriched spiking procedure, the concentration of Pb in procedure blanks was measured using external calibration. The externally calibrated procedure blank was measured twice.

5.2.2 Mass spectrometric measurement

Isotope dilution requires complete isotope mixing and equilibration, and the sample mixes must be diluted to optimal concentrations for introduction into the ICP-MS. Since all the Pb is in solution and has the same chemical form, the samples were simply thoroughly shaken to ensure mixing. Each sample was diluted to achieve a Pb concentration ~ 60 µg/l. Table 5.2 lists all the samples that were prepared for MS ratio measurement. The list shows the number of samples of each type and the measured ratios. It also identifies the isotope standard that was used for the mass bias correction factors for each MS ratio measurement.

Table 5.2 Summary of isotopic ratio measurements for the determination of Pb by IDMS.

Material	n*	Isotope Ratio(s) Measured	Comment	SRM for mass bias correction
Unknown solution	1	All isotopes, relative to 206	Isotopic Composition	981
Spike : unknown mix	4	208/206	Concentration of Unknown Solution by IDMS	982 through SpikeCal
Spike	1	All isotopes, relative to 206	Compare with certificate	981
Spike : assay std. mix	4	208/206	Spike calibration IDMS	982
Assay std.	1	All isotopes, relative to 206	Isotopic Composition	981
"Natural" isotopic standard SRM 981	1	208/206	Determine mass bias correction (F)	-
Equal-atom isotopic standard SRM 982	1	208/206	Determine mass bias correction (F)	-

n = number of solutions or mixtures to be prepared and measured on the MS instrument

Figure 5.1 identifies the seven types of ratio measurement required for the complete experiment. These are characterised by the "natural" isotopic composition measurement of the unknown and the assay standard; the isotopic composition of the spike; the mass bias correction measurements from the "natural" isotopic standard, SRM 981, the equal-atom standard, SRM 982; and the ratio measurements of the isotope dilution mixtures. It is best to measure ratios of approximately the same intensity together. It is especially

important to make sure that a thorough washout is done both before and after measurement of the 206 spike. These measurements are summarised in Table 5.2.

For the isotope dilution mixtures, the order of sample measurement was: 2% (v/v) nitric acid, SRM 982, SpikeCal3 (working isotopic control). The samples, blank, and spike calibrations were then run in random order with the working isotopic control bracketing every two samples. Each sample was typically introduced into the instrument for two minutes before the data were collected.

5.2.3 IDMS calculation

5.2.3.1 Mass bias correction factor and normalisation ratios

For measured 208/206 ratios, the correction factor for isotopic discrimination was calculated by:

$F_d(208) = F(208) + F_{bias}(208)$ where;

$F(208) = R_c(208)/R_m(208)$

where $F_d(208)$ is the mass bias correction factor for 208/206 ratios,

$F(208)$ is the mass bias correction factor for 208/206 ratios at time 0,

$F_{bias}(208)$ is a bias factor coming into effect as soon as the F factor is applied to correct a ratio measured at a different time during the measurement,

$R_c(208)$ is the certified 208/206 isotopic ratio,

$R_m(208)$ is the measured 208/206 isotopic ratio for the certified material.

Measured 208/206 ratios can be normalised to an appropriate isotopic standard following

$R_n(208) = F(208) \,.\, R_m(208)$

where the subscripts *m, c,* and *n* above are used to signify measured, certified, and normalised ratios, respectively. Ratios of the other isotopes should be measured and normalised in a similar way. Thus, $R_m(204)$ and $R_m(207)$ refer to measured 204/206 and

207/206 isotope ratios, respectively, and $R_n(204)$ and $R_n(207)$ refer to the corresponding normalised ratios.

Note that two complete sets of mass bias correction factors are obtained: one set based on measurements of SRM 981 and the other on SRM 982. As indicated in Table 5.2, the mass bias correction factors based on SRM 981 will be used for the sample corresponding to the natural isotopic standard, and the correction factors based on SRM 982 will be used for the samples corresponding to the blended samples.

The mass bias correction factors obtained, based on measurements of SRM 981, were calculated as:

$F(208) = 2.1681/2.12 = 1.0226887$

$F(207) = 0.91464/0.9054 = 1.0102054$

$F(204) = 0.059042/0.0595 = 0.9923025.$

The mass bias correction factors obtained, based on measurements of SRM 982, were calculated as:

$F(208) = 1.00016/0.9781 = 1.0225539$

$F(207) = 0.46707/0.4627 = 1.0094446$

$F(204) = 0.027219/0.0274 = 0.9933942.$

Relative isotopic abundances, expressed in terms of atom fractions, $A_f(208)$, $A_f(207)$, $A_f(206)$, and $A_f(204)$, were calculated as follows:

$$A_f(208) = R_n(208) / [1 + R_n(208) + R_n(207) + R_n(204)]$$

$$A_f(207) = R_n(207) / [1 + R_n(208) + R_n(207) + R_n(204)]$$

$$A_f(206) = 1 / [1 + R_n(208) + R_n(207) + R_n(204)]$$

$$A_f(204) = R_n(204) / [1 + R_n(208) + R_n(207) + R_n(204)]$$

Relative atomic masses are given by:

$$M = [207.976641 \times A_f(208)] + [206.975885 \times A_f(207)] + [205.974455 \times A_f(206)] + [203.973037 \times A_f(204)].$$

5.2.3.2 Calculation for standard assay solution

The isotope ratios measured for the standard assay solution were as follows:

Isotope ratios	Ratios
204/206	0.0599
207/206	0.9059
208/206	2.116

The measurement isotope ratios can be normalised as follows:

$R_n(208) = (2.1160)(1.0225539) = 2.1637241$

$R_n(207) = (0.9059)(1.0094446) = 0.9144558$

$R_n(204) = (0.0599)(0.9923025) = 0.0594389$

Relative isotopic abundances, expressed in terms of atom fractions, $A_f(\ )$, were calculated as follows:

$A_f(208) = 2.1637241/(1 + 2.1637241 + 0.9144558 + 0.0594389)$

$= 0.5229394$

$A_f(207) = 0.9144558/(1 + 2.1637241 + 0.9144558 + 0.0594389)$

$= 0.2210102$

$A_f(206) = 1/(1 + 2.1637241 + 0.9144558 + 0.0594389)$

$= 0.2416849$

$A_f(204) = 0.0594389/(1 + 2.1637241 + 0.9144558 + 0.0594389)$

$= 0.0143655$

The relative atomic mass of Pb was determined as follows:

M = (*207.976641* x 0.5229394) + (*206.975885* x 0.2210102)

+ (*205.974455* x 0.2416849) + (*203.973037* x 0.0143655).

= 207.21405

The concentration of Pb in the assay standard solution Assay2 (c_z) was calculated according to the equation:

c_z = *(m1.m2.w)/(d1.d2.M)*

= [(1.272 g)(0.1552 g)(0.999)]/[(1000 g)(100.5902 g)(207.21405 g/mol)]

= 9.47×10^{-9} mol/g

= 0.00947 µmol/g

5.2.3.3 Calculation for unknown solution

The isotope ratios measured on the unknown solution were as follows:

Isotope ratios	Ratios
204/206	0.0549
207/206	0.8422
208/206	2.049

The measurement isotope ratios can be normalised as follows:

$R_n(208)$ = (2.0490) (1.0226887) = 2.0954891

$R_n(207)$ = (0.8422) (1.0102054) = 0.8507950

$R_n(204)$ = (0.0549) (0.9923025) = 0.0544774

Relative isotopic abundances, expressed in terms of atom fractions, $A_f(\ \ )$, were calculated as follows:

$A_f(208)$ = 2.0954891 / (1 + 2.0954891 + 0.8507950 + 0.0544774)

= 0.5237726

$A_f(207)$ = 0.8507950 / (1 + 2.0954891 + 0.8507950 + 0.0544774)

= 0.2126583

$A_f(206)$ = 1 / (1 + 2.0954891 + 0.8507950 + 0.0544774)

= 0.2499524

$A_f(204)$ = 0.0544774 / (1 + 2.0954891 + 0.8507950 + 0.0544774)

= 0.0136168

The relative atomic mass of Pb was determined as follows:

M = (*207.976641* x 0.5237726) + (*206.975885* x 0.2126583)

+ (*205.974455* x 0.2499524) + (*203.973037* x 0.0136168).

= 207.20885

5.2.3.4 Calculation for spike : cal1 solution

The isotope ratios measured on spike : cal1 solution were as follows:

Isotope ratios	Ratios
204/206	0.0127
207/206	0.2445
208/206	0.4509

The measurement isotope ratios can be normalised as follow:

$R_n(208)$ = (0.4509) (1.0225539) = 0.4610696

$R_n(207)$ = (0.2445) (1.0094446) = 0.2468092

$R_n(204)$ = (0.0127) (0.9933942) = 0.0126161

Relative isotopic abundances, expressed in terms of atom fractions, $A_f(\quad)$, were calculated as follows:

$A_f(208)$ = 0.4610696 / (1 + 0.4610696 + 0.2468092 + 0.0126161)

= 0.2679866

$A_f(207)$ = 0.2468092 / (1 + 0.4610696 + 0.2468092 + 0.0126161)

= 0.1434524

$A_f(206)$ = 1 / (1 + 0.4610696 + 0.2468092 + 0.0126161)

= 0.5812281

$A_f(204)$ = 0.0126161 / (1 + 0.4610696 + 0.2468092 + 0.0126161)

= 0.0073328

The Pb concentration of the spike solution (Spike : cal1) was calculated from the results of the "reverse isotope dilution" as follows:

$$C_{spike} = \frac{M_{assay} \times C_{assay}}{M_{spike}} \times \left(\frac{A_f(208, assay) - R_n(208, SpikeCal) \times A_f(206, assay)}{R_n(208, SpikeCal) \times A_f(206, spike) - A_f(208, spike)} \right)$$

where C_{spike} is the concentration of total Pb in the spike solution; M_{spike} and M_{assay} are the masses of spike solution and assay standard solution, respectively, that were mixed together to create the spike : assay standard mix; and C_{assay} is the concentration of Pb in the assay standard solution. The isotope ratio in this equation, denoted $R_n(208, SpikeCal)$, is the normalised $R(208)$ ratio for the spike calibration mix. Two sets of atom fractions are used. $A_f(206, assay)$ and $A_f(208, assay)$ denote the calculated 206 and 208 atom fractions for the assay standard Pb, as obtained from the isotope ratio measurements corresponding to the isotopic composition in the assay standard. On the other hand, $A_f(206, spike)$ and $A_f(208, spike)$ refer to the atom fractions for the spike solution in the certificate rather than the measurement values. Although the measured fractions are subject to instrument bias and the certified fractions can be of variable metrological quality, the effects of these bias sources cancel in the final calculation of the unknown sample concentration.

$$C_{spike1} = \frac{1.013 \times 0.00947}{0.9881} \times \left(\frac{0.5229394 - 0.4610696 \times 0.2416849}{0.4610696 \times 0.9214968 - 0.0125499} \right)$$

$\therefore C_{spike1} = 0.00969$ μmol/g

Four results for Pb concentration in the other "spike solution" determined by reverse isotope dilution were calculated by the same procedure and shown below.

C_{spike1} (μmol/g)	C_{spike2} (μmol/g)	C_{spike3} (μmol/g)	C_{spike4} (μmol/g)	Mean (μmol/g)	±	1SD
0.00969	0.00970	0.00970	0.00969	0.00969	±	0.00001

5.2.3.5 Calculation for spike : unk1 solution

The isotope ratios measured on spike : unk1 solution were as follows:

Isotope ratios	Ratios
204/206	0.0105
207/206	0.2133
208/206	0.3888

The measurement isotope ratios can be normalised as follows:

$R_n(208)$ = (0.3888) (1.0225539) = 0.3975690

$R_n(207)$ = (0.2133) (1.0094446) = 0.2153145

$R_n(204)$ = (0.0105) (0.9933942) = 0.0104306

Relative isotopic abundances, expressed in terms of atom fractions, $A_f(\ )$, were calculated as follows:

$A_f(208)$ = 0.3975690 / (1 + 0.3975690 + 0.2153145 + 0.0104306)

= 0.2449119

$A_f(207)$ = 0.2153145 / (1 + 0.3975690 + 0.2153145 + 0.0104306)

= 0.1326389

$A_f(206)$ = 1 / (1 + 0.3975690 + 0.2153145 + 0.0104306)

= 0.6160237

$A_f(204)$ = 0.0104306 / (1 + 0.3975690 + 0.2153145 + 0.0104306)

= 0.0064255

The Pb concentration in the unknown solution, corrected for blank, is calculated as follows:

$$C_{unk} = \frac{M_{spike} * C_{spike}}{M_{unk}} \times \left(\frac{R_n(208, spike:unknown) \times A_f(206, spike) - A_f(208, spike)}{A_f(208, unknown) - R_n(208, spike:unknown) \times A_f(206, unknown)} \right) - C_{blank}$$

where

$M_{unknown}$ = the mass of the unknown solution

= 1.0113 g

M_{spike} = the mass of spike solution

= 1.0176 g

C_{spike} = the calculated concentration of spike solution

= 0.00969 μmol/g

R_n (208, spike : unknown) = the normalised R(208) ratio obtained from the spike : unknown mix

= 0.397569

$A_f(208, unknown)$ = the calculated atom fraction for the "natural" lead in unknown sample, obtained from the isotope ratio measurements

= 0.5237726

$A_f(206, unknown)$ = the calculated atom fraction for the "natural" lead in unknown sample, obtained from the isotope ratio measurements

= 0.2499524

$A_f(206, spike)$ = the certified atom fraction for the spike

= 0.9214968

$A_f(208, spike)$ = the certified atom fraction for the spike

= 0.0125499

C_{blank} = Pb concentration (μmol/g) of blank determined by ICP-OES

= 0.000067 ± 0.000023 μmol/g

$$C_{unknown1} = \frac{1.0176 \times 0.00969}{1.0113} \times \left(\frac{0.397569 \times 0.9214968 - 0.0125499}{0.5237726 - 0.397569 \times 0.2499524} \right) - 0.000067$$

$C_{unknown1}$ = 0.00806 μmol/g

By adopting the above calculation procedure, the Pb concentrations in spike: unk2, spike: unk3 and spike : unk4 were calculated, as shown below.

$C_{unknown1}$ (μmol/g)	$C_{unknown2}$ (μmol/g)	$C_{unknown3}$ (μmol/g)	$C_{unknown4}$ (μmol/g)	Mean (μmol/g)	±	1SD
0.00806	0.00807	0.00803	0.00801	0.00804	±	0.00003

The value of $C_{unknown}$ from this equation is expressed in μmoles per gram of solution. This concentration is converted to units of grams of Pb per gram of solution by multiplying by the relative atomic mass of Pb in the unknown solution. Thus, if we denote by $C_{unknown*}$ the concentration after conversion to unit of grams per gram,

$C_{unknown*}$ = $C_{unknown}$ x $M(unknown)$

where $M(unknown)$ is the calculated relative atomic mass of Pb in the unknown, based on the isotope ratio measurements.

$\therefore C_{unknown*}$ = 0.00804 x 207.20885

= 1.663 μg/g

5.2.4 Calculation of uncertainty of Pb concentration

The uncertainty assigned to the Pb concentration in the digested unknown sample solution was estimated following guidelines given in the EURACHEM / CITAC Guide Quantifying Uncertainty in Analytical Measurement (EURACHEM/CITAC, 2000). In accord with these guidelines, the uncertainties associated with the F-factors and the concentrations of the standard assay solution were treated separately.

5.2.4.1 Uncertainty on the F-factors

Using the values of *F(208, unknown)*, as an example, gives for F:

$$F(208, unknown) = R_c(208, unknown) / R_m(208, unknown)$$

$$= 2.1681 / 2.12$$

$$= 1.0226887$$

The certified isotope ratio 208/206 in the certificate for SRM 981 has a stated uncertainty of 0.0008 based on a 95% confidence interval (Table 5.1b). This value was converted to standard uncertainty by dividing by 2. This gives a standard uncertainty of u($R_c(208)$) = 0.0004. The measured isotope ratio 208/206 has a standard uncertainty of 0.000776 (as RSD). For the F-factor, the combined uncertainty can be calculated as:

$$\frac{u_c(F(208,unknown))}{F(208,unknown)} = \sqrt{\left(\frac{0.0004}{2.1681}\right)^2 + (0.000776)^2}$$

$$= 0.0007976$$

5.2.4.2 Uncertainty on F_{bias}

This bias factor is introduced to account for possible deviations in the value of the mass discrimination factor and is associated with every F-factor. The values of these biases are not known and, according to the EURACHEM / CITAC Guide, a value of 0 is applied. An uncertainty is associated with every bias and this has to be taken into consideration when calculating the final uncertainty. To reduce the complexities of this calculation, the uncertainties assigned to these biases were taken from the EURACHEM / CITAC Guide, which, based on long experience of Pb IDMS, were 0.001.

5.2.4.3 Uncertainty of the weighed masses

In this case, the normal weighing process was carried out. The calibration/linearity of the utilised balance will be taken into account in the calculation of the uncertainties of the weighed masses.

5.2.4.3.1 Uncertainty of $m_{unknown}$, m_{spike}, and m_{assay}

Calibration/linearity: The balance manufacturer quotes ±0.2 mg for the linearity contribution. This value represents the maximum difference between actual mass on the pan and the reading of the scale. The linearity contribution is assumed to show a rectangular distribution and is converted to a standard uncertainty:

$$\frac{0.2\ mg}{\sqrt{3}} \quad = \quad 0.115 \text{ mg}$$

The contribution for the linearity has to be accounted for twice, once for the tare and once for the gross mass, leading to an uncertainty $u(m_{Sample})$ of

$$u(m) \quad = \quad \sqrt{2 \times (0.115)^2}$$

$$= \quad 0.163 \text{ mg}$$

Note 1: The contribution is applied twice because no assumptions are made about the form of the non-linearity. The non-linearity is accordingly treated as a systematic effect on each weighing, which varies randomly in magnitude across the measurement range.

Note2: Buoyancy correction is not considered because all weighing results are quoted on the conventional basis for weighing in air. The remaining uncertainties are too small to consider.

5.2.4.4 Uncertainty in the Pb concentration of the standard assay solution, c_z

5.2.4.4.1 Uncertainty in the relative atomic mass of Pb

The combined uncertainty of the relative atomic mass of the assay solution, Assay, was calculated according to values given in Table 5.3.

Table 5.3 Data for calculation of the relative atomic mass of Pb in the standard assay solution.

	Value	Standard Uncertainty	Type
F_{bias}(208, 207, 206, 204, assay)	0	0.001	B
R_m(208, assay)	2.116	0.00071	A
F(208, assay)	1.0225539	0.0007336	A
F(207, assay)	1.0094446	0.0006842	A
F(204, assay)	0.9923025	0.0003133	A
R_m(206, assay)	1	0	A
R_m(207, assay)	0.9059	0.00066	A
R_m(204, assay)	0.0599	0	A
M1	207.97664	0.000003	B
M2	205.97445	0.000003	B
M3	206.97588	0.000003	B
M4	203.97303	0.000003	B

The spreadsheet was used to calculate the combined standard uncertainty of the relative atomic mass of Pb in the standard assay solution. This gave a relative atomic mass M(Pb, assay) = 207.21405 g/mol with an uncertainty of 0.00399 g/mol. The calculation is shown in Table 5.4.

Table 5.4 The spreadsheet model for calculating the combined standard uncertainty of the relative atomic mass of Pb in the standard assay solution.

		U(Fbias(assay, i)	Rm(208, assay)	F(208, assay)	F(207, assay)	F(204, assay)	Rm(206, assay)	Rm(207, assay)	Rm(204, assay)	M1	M2	M3	M4
		0.001	0.00071	0.00073358	0.00068421	0.00031334	0	0.00066	0	0.000003	0.000003	0.000003	0.000003
	Value												
Fbias(assay, i)	0	0.001	0	0	0	0	0	0	0	0	0	0	0
Rm(208, assay)	2.116	2.1429	2.1483	2.1429	2.1429	2.1429	2.1429	2.1429	2.1429	2.1429	2.1429	2.1429	2.1429
F(208, assay)	1.0225539	0.9989	0.9989	1.0014	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989
F(207, assay)	1.0094446	0.9993	0.9993	0.9993	1.0028	0.9993	0.9993	0.9993	0.9993	0.9993	0.9993	0.9993	0.9993
F(204, assay)	0.9923025	1.0002	1.0002	1.0002	1.0002	1.0062	1.0002	1.0002	1.0002	1.0002	1.0002	1.0002	1.0002
Rm(206, assay)	1	1	1	1	1	1	1	1	1	1	1	1	1
Rm(207, assay)	0.9059	0.9147	0.9147	0.9147	0.9147	0.9147	0.9147	0.9179	0.9147	0.9147	0.9147	0.9147	0.9147
Rm(204, assay)	0.0599	0.0587	0.0587	0.0587	0.0587	0.0587	0.0587	0.0587	0.05905	0.0587	0.0587	0.0587	0.0587
M1	207.976636	207.976636	207.976636	207.976636	207.976636	207.976636	207.976636	207.976636	207.976636	207.976639	207.976636	207.976636	207.976636
M2	205.974449	205.974449	205.974449	205.974449	205.974449	205.974449	205.974449	205.974449	205.974449	205.974449	205.974452	205.974449	205.974449
M3	206.97588	206.97588	206.97588	206.97588	206.97588	206.97588	206.97588	206.97588	206.97588	206.97588	206.97588	206.975883	206.97588
M4	203.973028	203.973028	203.973028	203.973028	203.973028	203.973028	203.973028	203.973028	203.973028	203.973028	203.973028	203.973028	203.973031
M(Pb, assay)	207.214047	207.210345	207.211348	207.211342	207.2101625	207.210068	207.2103448	207.2101627	207.2100693	207.210346	207.210346	207.210345	207.210345
u(y, xi)		-0.00370179	0.00100357	0.00099673	-0.00018235	-0.00027717	0	-0.000182135	-0.000275493	1.5612E-06	7.2934E-07	6.6666E-07	4.2821E-08
u(y)2, u(y,xi)2		1.3703E-05	1.0072E-06	9.9348E-07	3.32498E-08	7.6823E-08	0	3.31733E-08	7.58966E-08	2.4373E-12	5.3194E-13	4.4443E-13	1.8336E-15
uc(M)	0.00399036												

5.2.4.4.2 Calculation of the combined standard uncertainty in determining c_z

All parameters used in the calculation of the concentration of Pb in the standard assay solution were identified along with the uncertainty, calculated from the following data.

	Value	Uncertainty
Mass of lead piece, m1 (g)	1.272	0.002
Total mass first dilution, d1 (g)	1000	0.0163
Aliquot of first dilution, m2 (g)	0.1552	0.000163
Total mass of second dilution, d2 (g)	100.5902	0.000163
Purity of metallic lead piece, w (mass fraction)	0.9999	0.0005
Molar mass of Pb in the Assay material, M (g/mol)	207.21405	0.00399

The spreadsheet shown in Table 5.5 was used to calculate the combined standard uncertainty of the concentration of Pb in the standard assay solution. This gave a concentration of Pb in the standard assay solution c_z = 0.00947 μmol/g, with uncertainty of 0.00001852 μmol/g (Table 5.5).

Table 5.5 The spreadsheet model for calculating the combined standard uncertainty of the concentration of Pb in the standard assay solution.

		U (m1)	u(d1)	u(m2)	u(d2)	u(w)	u(M)
		0.002	0.0163	0.000163	0.000163	0.0005	0.00399
	Value						
Mass of lead piece, m1 (g)	1.272	1.274	1.272	1.272	1.272	1.272	1.272
Total mass first dilution, d1 (g)	1000	1000	1000.0163	1000	1000	1000	1000
Aliquot of first dilution, m2 (g)	0.1552	0.1552	0.1552	0.155363	0.1552	0.1552	0.1552
Total mass of second dilution, d2 (g)	100.5902	100.5902	100.5902	100.5902	100.590363	100.5902	100.5902
Purity of metallic lead piece, w (mass fraction)	0.9999	0.9999	0.9999	0.9999	0.9999	1.0004	0.9999
Molar mass of Pb in the Assay material, M (g/mol)	207.21405	207.21405	207.21405	207.21405	207.21405	207.21405	207.21804
Cz	9.47023E-09	9.48512E-09	9.47008E-09	9.48018E-09	9.47021E-09	9.47497E-09	9.47005E-09
u(y, xi)		1.48903E-11	-1.54362E-13	9.94618E-12	-1.53459E-14	4.73559E-12	-1.8235E-13
u(y)2, u(y,xi)2		2.21721E-22	2.38277E-26	9.89265E-23	2.35496E-28	2.24258E-23	3.32515E-26
$u(c_z)$ =	1.85238E-11						

5.2.4.5 Calculating the combined standard uncertainty

The spreadsheet model was applied to calculate $u_c(c_{unknown*})$ for replicate 1 of the determination of Pb by IDMS. The uncertainty budget for replicate 1 is representative for the measurement of all four replicates. The spreadsheet is not shown here because of the number of parameters used in the calculation. The values of the parameters and their uncertainties, as well as the combined uncertainty of $c_{unknown*}$, are listed in Table 5.6.

Table 5.6 The uncertainty budget for calculating $u_c(c_{unknown*})$ for the determination of Pb concentration in digested peat sample solutions by IDMS.

Parameter	Uncertainty evaluation	Value	Experimental uncertainty	Final uncertainty
F_{bias}	B	0	0.001	0.001
C_z	B	0.00947	1.852E-05	1.85E-05
F(208, spike:unknown1)	A	1.022554	0.0002976	0.000105
F(208, spike:cal1)	A	1.022554	0.0006082	0.000215
F(208, unknown)	A	1.022689	0.0007976	0.000282
F(207, unknown)	A	1.010205	0.0005118	0.000181
F(204, unknown)	A	0.992303	0.0011159	0.000395
F(208, spike)	A	1	0.0008811	0.000312
F(208, assay)	A	1.022689	0.00075	0.000265
F(207, assay)	A	1.010205	0.0006621	0.000234
F(204, assay)	A	0.992303	0.000876	0.00031
$m_{unknown}$	B	1.0113	0.000163	0.000163
$m_{spike/unknown}$	B	1.0176	0.000163	0.000163
$m_{spike/assay}$	B	0.9881	0.000163	0.000163
m_{assay}	B	1.013	0.000163	0.000163
R_m(208, spike:unknown1)	A	0.3888	0.000237	0.000084
R_m(208, spike:cal1)	A	0.4509	0.000581	0.000205
R_m(208, unknown)	A	2.049	0.000776	0.000274
R_m(206, unknown)	Cons	1	0	0
R_m(207, unknown)	A	0.8422	0.000479	0.000169
R_m(204, unknown)	A	0.0549	0.001071	0.000379
R_m(208, spike)	A	0.013619	0.0008811	0.000312
R_m(208, assay)	A	2.116	0.000727	0.000257
R_m(206, assay)	Cons	1	0	0
R_m(207, assay)	A	0.9059	0.000637	0.000225
R_m(204, assay)	A	0.0599	0.000818	0.000289
C_{blank}	A	0.000067	0.000051	0.000026
$C_{unknown}$		0.008061	0.0000568	0.000028

The mean and the experimental standard deviation from the determination of Pb in NIMT/UOE/FM/001 by IDMS of the four replicates are displayed below:

Replicate1 (µmol/g)		Mean of replicates1-4 (µmol/g)	
$C_{unknown}$	0.00806	$C_{unknown}$	0.00804
$u_c(C_{unknown})$	0.00006	S	0.00003

The concentration of Pb in the digested solution of the ombrotrophic peat bog reference material "NIMT/UOE/FM/001" with an expanded uncertainty using a coverage factor of 2 is then:

$C_{unknown}$ = 0.00804 ± 0.00011 µmol/g or

$C_{unknown*}$ = 1.663 ± 0.023 µg/g

To convert this value into the concentration of Pb expressed in units of w/w solid phase reference material, the following equation was applied:

$$C = \frac{C_{unknown} \times V_L}{m_{Sample}}$$

Where $C_{unknown*}$ = Concentration of the digested solution

= 1.663 µg/g

V_L = Weight of 25 ml solution in grams

= 24.825 g

m_{sample} = Dry weight (105°C) of sample

= 0.0002319 kg

C (mg/kg) = (1.663)(24.825) / 0.0002319

= 178.02 mg/kg

∴ Pb concentration in solid phase reference material corrected for moisture content = 178.02 mg/kg.

5.2.5 Estimation of uncertainty assigned to the Pb concentration in the solid phase

5.2.5.1 Identifying uncertainty sources

The identification of all relevant uncertainty sources for this analytical procedure is shown in a cause and effect diagram below. The parameters in the equation of measurand are represented by the main branches of the diagram. Further factors are added to the diagram, considering each step in the analytical procedure (Figure 5.2).

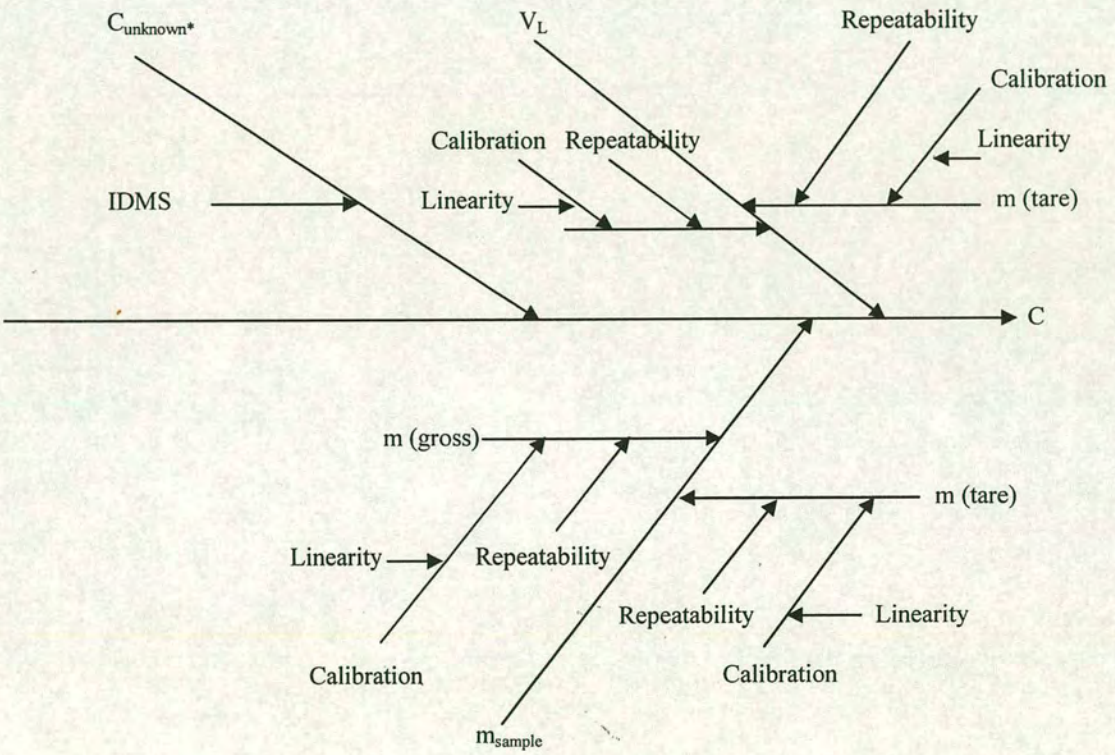


Figure 5.2 Cause and effect diagram for uncertainty calculation of Pb concentration in solid material.

5.2.5.2 Quantifying uncertainty sources

The aim of this step is to quantify the uncertainty arising from each of the previously identified sources.

5.2.5.2.1 Uncertainty of m_{Sample} [$u(m_{Sample})$]

Calibration/linearity: The balance manufacturer quotes ±2 mg for the linearity contribution. This value represents the maximum difference between actual mass on the pan and the reading of the scale. The linearity contribution is assumed to show a rectangular distribution and is converted to a standard uncertainty:

$$\frac{2\ mg}{\sqrt{3}} = 1.15\ \text{mg}$$

The contribution for the linearity has to be accounted for twice, once for the tare and once for the gross mass, leading to an uncertainty $u(m_{Sample})$ of

$$u(m_{Sample}) = \sqrt{2\times(1.15)^2}$$

$$= 1.63\ \text{mg}$$

Note 1: The contribution is applied twice because no assumptions are made about the form of the non-linearity. The non-linearity is accordingly treated as a systematic effect on each weighing, which varies randomly in magnitude across the measurement range.

Note2: Buoyancy correction is not considered because all weighing results are quoted on the conventional basis for weighing in air. The remaining uncertainties are too small to consider.

5.2.5.2.2 Uncertainty of weight for 25 ml solution V_L [$u(V_L)$]

Since the same balance was used for weighing digested sample solutions, uncertainties assigned to V_L were calculated in the same way as $u(m_{Sample})$. Therefore the $u(V_L)$ was 1.63 mg.

5.2.5.2.3 Uncertainty of metal concentration ($C_{unknown*}$) [$u_c(C_{unknown})$]

The Pb concentration calculated from the IDMS is

$C_{unknown*}$ = 1.663 ± 0.023 µg/g

The stated uncertainty was divided by 2 to give the standard uncertainty, i.e.

$u_c(C_{unknown})$ = 0.0115.

5.2.5.3 Calculating the combined standard uncertainty

The final Pb concentration in the solid phase reference material was calculated as 178.02 mg/kg. The intermediate values and their uncertainties are displayed in Table 5.7.

Table 5.7 The uncertainty budget for calculating Pb concentration in the solid peat reference material NIMT/UOE/FM/001 after analysis by IDMS.

$u_c(c)$	Descriptions	Value	Standard uncer. u(x)	Relative standard uncer. u(x)/x
$C_{unknown}$	Content of Pb in the digested solution (µg/g)	1.663	0.0115	0.00691
V_L	Volume (g)	24.825	0.00163	0.0000657
m_{Sample}	Mass (kg)	0.000237	0.00000163	0.0069

In order to calculate the combined standard uncertainty of this analytical result, the standard uncertainties of each component are used as follows:

$$\frac{u_c(c)}{c} = \sqrt{\left(\frac{u(c_0)}{c_0}\right)^2 + \left(\frac{u(V_L)}{V_L}\right)^2 + \left(\frac{u(m)}{m}\right)^2}$$

$$\frac{u_c(c)}{c} = \sqrt{(0.00691)^2 + (0.0000657)^2 + (0.0069)^2}$$

$$= 0.00976$$

$$u_c(c) = (0.00976)(178.02)$$

$$= 1.74 \text{ µg/g}$$

The expanded uncertainty *U(r)* is obtained by applying a coverage factor of 2

$U(r) = 1.74 \times 2$

$= 3.48\ \mu g/g$

$\therefore$ Pb concentration in solid phase reference material = 178 ± 3 mg/kg

5.3 Application of IDMS to the determination of Pb in the solid peat reference material

In this part of the experiment, the solid peat reference material NIMT/UOE/FM/001 was spiked with enriched ^{206}Pb isotope prior to being digested in the microwave digestion unit by the total digestion method (the adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat).

5.3.1 Sample preparation

5.3.1.1 Preparation of ^{206}Pb enriched spike solution (SRM 983)

The spike solution had previously been prepared to have a nominal concentration of ~150 mg/l. The 208/206 ratio was measured to confirm the identity and integrity of the spike.

The ~ 0.1 g piece of Pb metal (SRM 983) (99.9 % purity, *w*) (*m1*) was accurately weighed to ±0.1 mg. Then the piece of metal was dissolved in 10 ml of 1 : 3 w/w HNO_3 : H_2O on gentle heating. The solution was diluted in 2% v/v HNO_3 to a total mass of 100 g (*d1*). This solution was further diluted by accurately weighing 15 g solution (*m2*) to ±0.1 mg and then diluting in 2% (v/v) HNO_3 to a total mass of 100 g (*d2*). The weights used in the associated calculation are shown below:

$c_{spike} = (m1.m2.w)/(d1.d2.M)$

$= [(0.1113\ g)(15.0082\ g)(0.999)]/[(101.1951\ g)(100.8260\ g)(206.06\ g/mol)]$

$= 7.9799 \times 10^{-7}$ mol/g

$= 0.79799\ \mu mol/g$

5.3.1.2 Preparation of assay standard solution

In this experiment SRM 981 was used as assay standard. This solution was prepared by diluting the 1272 mg/l SRM 981 standard solution which had been prepared previously

by another analyst in the laboratory. The 1272 mg/l standard was prepared by dissolving a 1.272 g piece of Pb metal SRM 981 (*m1*) in 1 : 3 w/w HNO_3 : H_2O on gentle heating. The solution was then diluted in 2% v/v HNO_3 to a total mass of 1000 g (*d1*). This solution was named Assay1. A more dilute solution was needed, so an accurately weighed 15 g of Assay1 solution (*m2*) to ±0.1 mg was then diluted in 2% (v/v) HNO_3 to a total mass of 100 g (*d2*). This solution was named Assay2.

5.3.1.3 Preparation of unknown sample solution

The ombrotrophic peat reference material was spiked with enriched ^{206}Pb prior to being digested according to the adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat. It was known from previous experiments that the Pb concentration in this reference material was ~150 mg/kg, a value used in further calculation here. Three different sets of samples, spike : unknown sample mixtures, spike : assay standard mixtures, and unknown solution, were prepared. There were four replicate samples of spike : unknown sample mixtures, four replicate samples of spike : assay standard mixtures, and one sample of the unknown solution.

5.3.1.3.1 Preparation of spike : unknown sample mixtures

Four spike : unknown replicate sample mixtures were prepared as follows. A 0.25 g aliquot of solid peat sample was weighed, to an accuracy of ±0.1 mg, into clean beakers. To each sample aliquot was added a spike from the spike solution. The spike solution had been prepared to provide a concentration similar to that of the unknown sample solution, to enable approximately 1 : 1 mixing. The sample and the spike solution were physically mixed.

5.3.1.3.2 Preparation of spike : assay standard mixtures

At the same time as the spike : unknown sample mixtures were prepared, four 0.25 g aliquots of the spike solution were weighed into clean beakers so that the Pb concentration could be determined in the "spike calibration". The spike calibration is achieved by a "reverse isotope dilution" experiment against the four natural Pb solutions prepared from the assay standard.

The four spike: assay standard mixtures were named SpikeCal1, SpikeCal2, SpikeCal3, and SpikeCal4. The mixtures were prepared by 1 : 1 addition of the spike solution and the assay standard solution to beakers. The standard assay and the spike solution were then mixed together by shaking the beakers by hand.

5.3.1.3.3 Preparation of unknown solution

The unknown solution was prepared by weighing 0.25 g of solid peat reference material to an accuracy of ±0.1 mg into a clean beaker. No spike solution was added to this beaker.

The spike : unknown sample mixtures, spike : assay standard mixturees, and unknown solution were then ashed at 450 °C for 4 hours and then digested in the microwave digestion system according to the "adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat" (Section 3.2, Chapter 3). Finally, each sample was diluted to achieve an optimal Pb concentration of ~ 60 µg/l for introduction into the ICP-MS.

5.3.2 IDMS calculation

The mass bias correction factors, based on measurements of SRM 981, were calculated as follows:

F(208)	=	2.1681 / 2.1680	=	1.0000461
F(207)	=	0.91464 / 0.8394	=	1.0896355
F(204)	=	0.059042 / 0.0545	=	1.0833394.

Similarly, for SRM 982,

F(208)	=	1.00016 / 1.001	=	0.9991608
F(207)	=	0.46707 / 0.4291	=	1.0884875
F(204)	=	0.027219 / 0.0251	=	1.0844223.

5.3.2.1 Calculation for standard assay solution

The isotope ratios measured for the standard assay solution were as follows:

Isotope ratios	Ratios
204/206	0.0547
207/206	0.8395
208/206	2.167

The measurement isotope ratios can be normalised as follows:

$R_n(208)$ = (2.167) (0.9991608) = 2.1651818

$R_n(207)$ = (0.8395) (1.0884875) = 0.9137853

$R_n(204)$ = (0.0547) (1.0833394) = 0.0592587

Relative isotopic abundances, expressed in terms of atom fractions, $A_f(\ )$, were calculated as follows:

$A_f(208)$ = 2.1651818 / (1 + 2.1651818 + 0.9137853 + 0.0592587)

= 0.5232150

$A_f(207)$ = 0.9137853 / (1 + 2.1651818 + 0.9137853 + 0.0592587)

= 0.2208157

$A_f(206)$ = 1 / (1 + 2.1651818 + 0.9137853 + 0.0592587)

= 0.2416495

$A_f(204)$ = 0.0592587 / (1 + 2.1651818 + 0.9137853 + 0.0592587)

= 0.0143198

The relative atomic mass of Pb was determined as follows:

M = (*207.976641* x 0.5232150)+ (*206.975885* x 0.2208157)

+ (*205.974455* x 0.2416495) + (*203.973037* x 0.0143198).

= 207.21479

The concentration of Pb in the assay standard solution Assay2 (c_z) was calculated according to the equation:

c_z = $(m1.m2.w)/(d1.d2.M)$

= [(1.272 g)(15.0154 g)(0.999)]/[(1000 g)(100.7184 g)(207.21479 g/mol)]

= 9.1506×10^{-7} mol/g

= 0.91506 μmol/g

5.3.2.2 Calculation for unknown solution

The isotope ratios measured for the unknown solution were as follows:

Isotope ratios	Ratios
204/206	0.05
207/206	0.7756
208/206	2.08

The measurement isotope ratios can be normalised as follows:

$R_n(208)$ = (2.08) (1.0000461) = 2.0800959

$R_n(207)$ = (0.7756) (1.0896355) = 0.8451213

$R_n(204)$ = (0.05) (1.0833394) = 0.054167

Relative isotopic abundances, expressed in terms of atom fractions, $A_f(\quad)$, were calculated as follows:

$A_f(208)$ = 2.0800959 / (1 + 2.0800959 + 0.8451213 + 0.054167)

= 0.5227181

$A_f(207)$ = 0.8451213 / (1 + 2.0800959 + 0.8451213 + 0.054167)

= 0.2123749

$A_f(206)$ = 1 / (1 + 2.0800959 + 0.8451213 + 0.054167)

= 0.2512952

$A_f(204)$ = 0.054167 / (1 + 2.0800959 + 0.8451213 + 0.054167)

= 0.0136119

The relative atomic mass of Pb was determined as follows:

M = (*207.976641* x 0.5227181) + (*206.975885* x 0.2123749)

+ (*205.974455* x 0.2512952) + (*203.973037* x 0.0136119).

= 207.20647

5.3.2.3 Calculation for spike : cal1 solution

The isotope ratios measured on spike : cal1 solution were as follows:

Isotope ratios	Ratios
204/206	0.0125
207/206	0.2373
208/206	0.4921

The measurement isotope ratios can be normalised as follows:

$R_n(208)$ = (0.4921) (0.9991608) = 0.4916870

$R_n(207)$ = (0.2373) (1.0884875) = 0.2582981

$R_n(204)$ = (0.0125) (1.0844223) = 0.0135553

Relative isotopic abundances, expressed in terms of atom fractions, $A_f(\ )$, were calculated as follows:

$A_f(208)$ = 0.4916870 / (1 + 0.4916870 + 0.2582981 + 0.0135553)

= 0.2788068

$A_f(207)$ = 0.2582981 / (1 + 0.4916870 + 0.2582981 + 0.0135553)

= 0.1464656

$A_f(206)$ = 1 / (1 + 0.4916870 + 0.2582981 + 0.0135553)

$= \quad 0.5670412$

$A_f(204) \quad = \quad 0.0135553 / (1 + 0.4916870 + 0.2582981 + 0.0135553)$

$= \quad 0.0076864$

The Pb concentration of the spike solution (Spike : cal1) was calculated from the results of the "reverse isotope dilution" as follows:

$$C_{spike} = \frac{M_{assay} * C_{assay}}{M_{spike}} \times \left(\frac{A_f(208, assay) - R_n(208, SpikeCal) \times A_f(206, assay)}{R_n(208, SpikeCal) \times A_f(206, spike) - A_f(208, spike)} \right)$$

$$C_{spike1} = \frac{0.2507 \times 0.00915063}{0.2651} \times \left(\frac{0.523215 - 0.491687 \times 0.2416495}{0.491687 \times 0.9214968 - 0.0125499} \right)$$

$\therefore C_{spike1} \quad = \quad 0.79437 \quad \mu mol/g$

Four results for Pb concentration in the "spike solution" determined by reverse isotope dilution were calculated and shown in the table below.

C_{spike1} (μmol/g)	C_{spike2} (μmol/g)	C_{spike3} (μmol/g)	C_{spike4} (μmol/g)	Means (μmol/g)	±	1SD
0.79437	0.79701	0.79387	0.78424	0.79237	±	0.00559

5.3.2.4 Calculation for spike : unk1 solution

The isotope ratios measured for the spike : unk1 solution were as follows:

Isotope ratios	Ratios
204/206	0.0105
207/206	0.2112
208/206	0.4373

The measurement isotope ratios can be normalised as follows:

$R_n(208) \quad = \quad (0.4373)\ (0.9991608) \quad = \quad 0.4369330$

$R_n(207) \quad = \quad (0.2112)\ (1.0884875) \quad = \quad 0.2298860$

$R_n(204)$ = (0.0105) (1.0844223) = 0.0113864

Relative isotopic abundances, expressed in terms of atom fractions, $A_f(\ )$, were calculated as follows:

$A_f(208)$ = 0.4369330 / (1 + 0.4369330 + 0.2298860 + 0.0113864)

= 0.2603569

$A_f(207)$ = 0.2298860 / (1 + 0.4369330 + 0.2298860 + 0.0113864)

= 0.136845

$A_f(206)$ = 1 / (1 + 0.4369330 + 0.2298860 + 0.0113864)

= 0.5958737

$A_f(204)$ = 0.0113864 / (1 + 0.4369330 + 0.2298860 + 0.0113864)

= 0.0067849

The Pb concentration in the unknown solution, corrected for blank, is calculated as follows:

$$C_{unk} = \frac{M_{spike} * C_{spike}}{M_{unk}} \times \left(\frac{R_n(208, spike:unknown) \times A_f(206, spike) - A_f(208, spike)}{A_f(208, unknown) - R_n(208, spike:unknown) \times A_f(206, unknown)} \right) - C_{blank}$$

where

$M_{unknown}$ = the mass of the unknown solution

= 0.2501 g

M_{spike} = the mass of spike solution

= 0.2698 g

C_{spike} = the calculated concentration of spike solution

= 0.79237 µmol/g

R_n (208, spike : unknown) = the normalised R(208) ratio obtained from the spike : unknown mix

= 0.436933

$A_f(208, unknown)$ = the calculated atom fraction for the "natural" Pb in unknown sample, obtained from the isotope ratio measurements
= 0.5227181

$A_f(206, unknown)$ = the calculated atom fraction for the "natural" Pb in unknown sample, obtained from the isotope ratio measurements
= 0.2512952

$A_f(206, spike)$ = the certified atom fraction for the spike
= 0.9214968

$A_f(208, spike)$ = the certified atom fraction for the spike
= 0.0125499

C_{blank} = Pb concentration of blank (μmol/g)
= 0.000067 ± 0.000023 μmol/g

$$C_{unknown1} = \frac{0.2698 \times 0.79237}{0.2501} \times \left(\frac{0.436933 \times 0.9214968 - 0.0125499}{0.5227181 - 0.436933 \times 0.2512952} \right) - 0.000067$$

$\therefore C_{unknown1} =$ 0.80955 μmol/g

By adopting the above calculation procedure, the Pb concentrations in spike : unk2, spike : unk3 and spike : unk4 were calculated, as shown below:

$C_{unknown1}$ (μmol/g)	$C_{unknown2}$ (μmol/g)	$C_{unknown3}$ (μmol/g)	$C_{unknown4}$ (μmol/g)	Means (μmol/g)	±	1SD
0.80955	0.80797	0.81614	0.82613	0.81495	±	0.00825

The value of $C_{unknown}$ from this equation is expressed in μmoles per gram of solution. This concentration is converted to units of grams of Pb per gram of solution by multiplying by the relative atomic mass of Pb in the unknown solution. Thus, if we denote by $C_{unknown*}$ the concentration after conversion to units of grams per gram,

$$C_{unknown*} = C_{unknown} \times M(unknown)$$

where $M(unknown)$ is the calculated relative atomic mass of lead in the unknown, based on the isotope ratio measurements.

$\therefore C_{unknown*}$ = 0.81495 x 207.20666

= 168.86 µg/g

5.3.3 Calculation of uncertainty of Pb concentration

The uncertainty assigned to the Pb concentration in the digested unknown sample solution was estimated from guidelines given in the EURACHEM / CITAC Guide Quantifying Uncertainty in Analytical Measurement (EURACHEM / CITAC, 2000). In accord with these guidelines, the uncertainties associated with the F-factors and the concentration of the standard assay solutions were treated separately.

5.3.3.1 Uncertainty on the F-factors

Using the value of *F(208, unknown)*, as an example, gives for F:

F(208, unknown) = $R_c(208, unknown) / R_m(208, unknown)$

= 2.1681 / 2.1680

= 1.0000461

The certified isotope ratio 208/206 in the certificate for SRM 981 has a stated uncertainty of 0.0008 based on a 95% confidence interval. This value was converted to standard uncertainty by dividing by 2. This gives a standard uncertainty of u($R_c(208)$) = 0.0004. The measured isotope ratio 208/206 has a standard uncertainty of 0.001408 (as RSD). For the F-factor, the combined uncertainty can be calculated as:

$$\frac{u_c(F(208,unknown))}{F(208,unknown)} = \sqrt{\left(\frac{0.0004}{2.1681}\right)^2 + (0.001408)^2}$$

= 0.00142

5.3.3.2 Uncertainty on the F_{bias}

As before (Section 5.2.4.2, Chapter 5), the uncertainties assigned to these biases were taken as 0.001 from the EURACHEM / CITAC Guide.

5.3.3.3 Uncertainty of the weighed masses

In this case, the normal weighing process was carried out. The calibration/linearity of the utilised balance will be taken into account in the calculation of the uncertainties of the weighed masses.

5.3.3.3.1 Uncertainty of $m_{unknown}$, m_{spike}, and m_{assay}

Calibration/linearity: The balance manufacturer quotes ±0.2 mg for the linearity contribution. This value represents the maximum difference between actual mass on the pan and the reading of the scale. The linearity contribution is assumed to show a rectangular distribution and is converted to a standard uncertainty:

$$\frac{0.2\,mg}{\sqrt{3}} = 0.115 \text{ mg}$$

The contribution for the linearity has to be accounted for twice, once for the tare and once for the gross mass, leading to an uncertainty $u(m_{Sample})$ of

$$u(m) = \sqrt{2\times(0.115)^2}$$
$$= 0.163 \text{ mg}$$

5.3.3.4 Uncertainty in the concentration of the standard assay solution, c_z

5.3.3.4.1 Uncertainty in the relative atomic mass of Pb

The combined uncertainty of the relative atomic mass of the standard assay solution was calculated according to values in Table 5.8.

Table 5.8 Data for calculation of the relative atomic mass of Pb in the standard assay solution.

	Value	Standard Uncertainty	Type
F_{bias}(208, 207, 206, 204, assay)	0	0.001	B
R_m(208, assay)	2.167	0.002003	A
F(208, assay)	1.0000461	0.0015967	A
F(207, assay)	1.0896355	0.0013412	A
F(204, assay)	1.0833394	0.0032024	A
R_m(206, assay)	1	0	A
R_m(207, assay)	0.8395	0.002369	A
R_m(204, assay)	0.0547	0.004221	A
M1	207.97664	0.000003	B
M2	205.97445	0.000003	B
M3	206.97588	0.000003	B
M4	203.97303	0.000003	B

The spreadsheet was used to calculate the combined standard uncertainty of the relative atomic mass of Pb in the standard assay solution. This gave a relative atomic mass M(Pb, assay) = 207.21405 g/mol with an uncertainty of 0.00399 g/mol.

5.3.3.4.2 Uncertainty of the combined standard uncertainty in determining c_z

All parameters used in the calculation of the concentration of Pb in the standard assay solution were identified along with the uncertainty, calculated from the following data.

	Value	Uncertainty
Mass of lead piece, m1 (g)	1.272	0.002
Total mass first dilution, d1 (g)	1000	0.0163
Aliquot of first dilution, m2 (g)	15.0154	0.000163
Total mass of second dilution, d2 (g)	100.7184	0.000163
Purity of metallic lead piece, w (mass fraction)	0.9999	0.0005
Molar mass of Pb in the Assay material, M (g/mol)	207.21479	0.0046906

The spreadsheet as shown in Table 5.9 was used to calculate the combined standard uncertainty of the concentration of Pb in the standard assay solution. This gave a concentration of Pb in the standard assay solution c_z = 0.915063 μmol/g, with an uncertainty of 0.00151 μmol/g (Table 5.9).

Table 5.9 The spreadsheet model for calculating the combined standard uncertainty of the concentration of Pb in the standard assay solution.

		u (m1)	u(d1)	u(m2)	u(d2)	u(w)	u(M)
		0.002	0.0163	0.000163	0.000163	0.0005	0.0046906
	Value						
Mass of lead piece, m1 (g)	1.272	1.274	1.272	1.272	1.272	1.272	1.272
Total mass first dilution, d1 (g)	1000	1000	1000.0163	1000	1000	1000	1000
Aliquot of first dilution, m2 (g)	15.0154	15.0154	15.0154	15.015563	15.0154	15.0154	15.0154
Total mass of second dilution, d2 (g)	100.7184	100.7184	100.7184	100.7184	100.718563	100.7184	100.7184
Purity of metallic lead piece, w (mass fraction)	0.9999	0.9999	0.9999	0.9999	0.9999	1.0004	0.9999
Molar mass of Pb in the Assay material, M (g/mol)	207.2147925	207.2147925	207.2147925	207.2147925	207.2147925	207.2147925	207.2194831
Cz	9.15063E-07	9.16502E-07	9.15048E-07	9.15073E-07	9.15062E-07	9.15521E-07	9.15042E-07
u(y, xi)		1.4387784E-09	-1.49153E-11	9.9334866E-12	-1.48091E-12	4.5757728E-10	-2.07132E-11
u(y)2, u(y,xi)2		2.07008E-18	2.22466E-22	9.86741E-23	2.19309E-24	2.09376E-19	4.29038E-22
$u(c_z)$ =	1.51004E-09						

5.3.3.5 Calculation of the combined standard uncertainty

The spreadsheet model was applied to calculate $u_c(c_{unknown*})$ for replicate 1 of the determination of Pb in the solid peat material by IDMS. The uncertainty budget for replicate 1 is representative for the measurement of all four replicates. The spreadsheet is not shown here because of the number of parameters used in the calculation. The values of the parameters and their uncertainties, as well as the combined uncertainty of $c_{unknown*}$, are listed in Table 5.10.

Table 5.10 The uncertainty budget for calculating $u_c(c_{unknown*})$ for the determination of Pb concentration in solid peat material by IDMS.

Parameter	Uncertainty evaluation	Value	Experimental uncertainty	Final uncertainty
F_{bias}	B	0	0.001	0.001
C_z	B	0.915063036	0.00151	0.00151
F(208, spike:unknown1)	A	0.9991608	0.0011986	0.000424
F(208, spike:cal1)	A	0.9991608	0.0064725	0.002288
F(208, unknown)	A	1.000046125	0.00142	0.000502
F(207, unknown)	A	1.089635454	0.0006227	0.00022
F(204, unknown)	A	1.08333945	0.0028354	0.001002
F(208, spike)	A	1	0.0008811	0.000312
F(208, assay)	A	1.000046125	0.0015967	0.000565
F(207, assay)	A	1.089635454	0.0013412	0.000474
F(204, assay)	A	1.08333945	0.0032024	0.001132
$m_{unknown}$	B	0.2501	0.000163	0.000163
$m_{spike/unknown}$	B	0.2698	0.000163	0.000163
$m_{spike/assay}$	B	0.2651	0.000163	0.000163
m_{assay}	B	0.2507	0.000163	0.000163
R_m(208, spike:unknown1)	A	0.4373	0.001185	0.000419
R_m(208, spike:cal1)	A	0.4921	0.00647	0.002287
R_m(208, unknown)	A	2.081	0.001149	0.000406
R_m(206, unknown)	Cons	1	0	0
R_m(207, unknown)	A	0.7756	0.002145	0.000758
R_m(204, unknown)	A	0.05	0.002337	0.000826
R_m(208, spike)	A	0.013619	0.0008811	0.000312
R_m(208, assay)	A	2.167	0.002003	0.000708
R_m(206, assay)	Cons	1	0	0
R_m(207, assay)	A	0.8395	0.002369	0.000838
R_m(204, assay)	A	0.0547	0.004221	0.001492
C_{blank}	A	0.000067	0.000051	0.000026
$C_{unknown}$		0.80956	0.01602	0.008008

The mean and the experimental standard deviation from the four replicates are displayed below:

Replicate1 (μmol/g)		Mean of replicates1-4 (μmol/g)	
$C_{unknown}$	0.80956	$C_{unknown}$	0.81495
$u_c(C_{unknown})$	0.01602	S	0.00825

The total Pb concentration in the digested solution of the ombrotrophic peat bog reference material "NIMT/UOE/FM/001", corrected for moisture content, (with an expanded uncertainty using a coverage factor of 2) is then:

$C_{unknown}$ = 0.81495 ± 0.01602 μmol/g or

$C_{unknown*}$ = 169 ± 7 mg/kg

Pb concentration in solid phase reference material = 169 ± 7 mg/kg.

5.4 Comparison of the Pb concentrations data obtained by IDMS on spiked digest solutions and solid phase peat

Analytical results obtained from the application of IDMS to determine the Pb concentration in the peat reference material "NIMT/UOE/FM/001" carried out after spiking the digest solutions and the solid material, are shown in Table 5.11, along with the Pb concentration obtained from the inter-laboratory comparison certification campaign.

Table 5.11 Comparison of total Pb concentration (expressed as concentration, mg/kg, corrected for moisture content, with an uncertainty using a coverage factor of 2) in ombrotrophic peat bog reference material NIMT/UOE/FM/001 derived from inter-laboratory comparison certification exercise, IDMS performed on the digest solution sample, and IDMS performed on the solid peat reference material.

Total Pb concentration (mg/kg)		
Inter-laboratory comparison	**IDMS on the digested peat solution sample**	**IDMS on the solid peat material**
174 ± 8	178 ± 3	169 ± 7

It can be seen that the Pb concentration in the ombrotrophic peat reference material determined by IDMS on both a digest solution and the solid peat sample itself are close to the certified value acquired by the inter-laboratory comparison (Table 4.10, Chapter 4). The uncertainties of the Pb concentrations were calculated according to the guidelines of the EURACHEM/CITAC Guide Quantifying Uncertainty in Analytical Measurement. The uncertainty assigned to the Pb concentration value obtained from the digest solution is lower than the one for the solid peat material. The major advantage of IDMS applied to the solid peat material is that the uncertainties arising during the digestion and analytical procedures were included throughout the process. Any contamination and subsequent losses of Pb during the analytical procedure do not affect the result obtained by IDMS on solid peat material.

In conclusion, this study established that the application of the IDMS method to the determination of Pb in the solid peat reference material provides accurate analytical results.

Chapter 6

Application of Methods to Flanders Moss Peat Cores

This chapter focuses on the determination, comparison and interpretation of vertical profiles of inorganic elements in two peat cores from Flanders Moss peat bog. The cores were collected by different methods in July 1999 (monolith; Section 3.3 of Chapter 3) and September 2001 (as described in this Chapter).

6.1 Description of Flanders Moss peat bog

Flanders Moss bog is located in the central belt of Scotland, 16 km west of Stirling (Fig. 6.1). Covering an area of 859.06 ha, Flanders Moss is the remnants of one of the largest active raised bog complexes in Britain. East Flanders Moss is the largest raised bog in the UK that is still in a predominantly near-natural state. The Flanders Moss site, with 548 ha of active raised bog, has 13.7% of the total area of those left in Britain (and 2.8% of that in the EU) (SNH, 2001). It contains a number of important raised bog features such as endotelmic streams (where the bog is the main source of the water), rand (steep slope at the bog's edge) and intact lagg (wetland beyond the edge of the bog). Drier areas are dominated by ling *Calluna vulgaris*, cross-leaved heath *Erica tetralix*, and cotton-grass *Eriophorum vaginatum*. Where the bog surface is wetter, plant communities dominated by actively growing bog-moss, notably *Sphagnum magellanicum* and *S. papillosum*, occur. The locally distributed mosses *S. imbricatum* and *S. molle* are also found here. Hydrologically, Flanders Moss comprises two main areas: one large single peat dome to the south west of the High Moss Pow and a three-dome complex to the east, with the main ridge running parallel to the Pow and watersheds branching northwards into the three domes partially separated by seepage lines. The northern area acts as a single functional peat dome. The hydrological connection between the two main domes of the moss is through peat of approx. 1 m in depth in the headwater stretch of the High Moss Pow.

Map from http://www.jncc.gov.uk/protectedsites/sacselection/sac.asp?EUcode=UK0012902

Figure 6.1 Location of Flanders Moss

6.2 Collection of 2001 core from Flanders Moss peat bog

Vegetation, consisting mainly of grass and perhaps a little *Sphagnum* moss, to a depth of ~ 10 cm on top of the bog was removed using a stainless steel knife and the peat core was collected using a Cuttle and Malcolm (1979) corer of dimensions 5 cm x 5 cm x 100 cm. Figure 6.2 shows the location of the site on the bog where the core was collected. The following visual observations were made: pale *Sphagnum* moss from top of the core to 2 cm; dark brown colour to 30 cm; paler colour from 30-38 cm; orange-coloured tinge from 38 - 45 cm; darker colour to 53 cm; orange-coloured tinge to 76 cm; and wetter to the bottom (~ 1 m) (Fig. 6.3). The core was then sectioned into 2-cm slices using a knife. Each section was placed in a labelled polyethylene bag which was then sealed. The bags were transported to the laboratory.

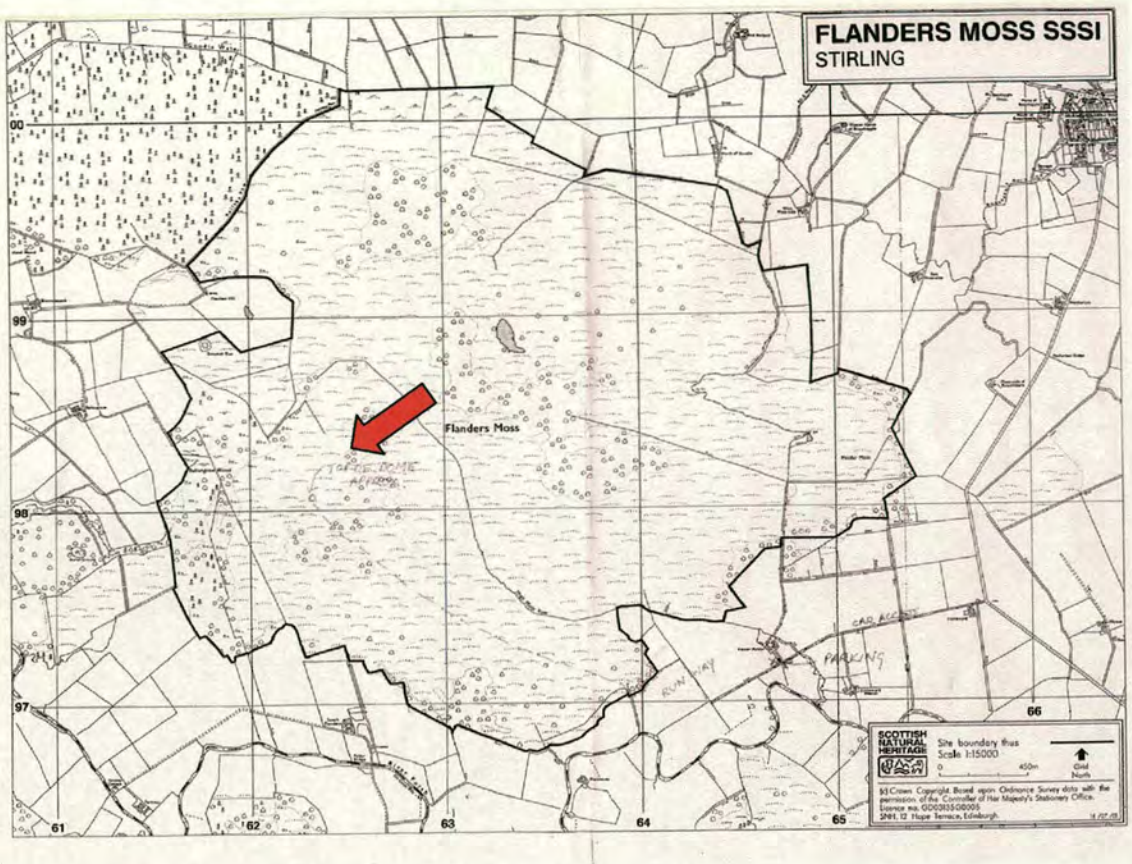


Figure 6.2 Location of the sampling site on Flanders Moss bog.

Figure 6.3 Flanders Moss peat core collected on 11/09/2001. Top of the core is to the left.

6.3 Laboratory handling and physical pre-treatment of 2001 peat core samples

Each section of peat material was weighed to obtain the wet weight and subsequently air-dried in pre-cleaned Teflon boats for 3-4 weeks. After weighing to obtain the dry weight, the sections were then ground by hand using a mortar and pestle to < 2 mm. Each section of powdered peat material was then stored in a 15 ml Sterilin tube, ready for analysis. The wet weight, air-dried weight, water content (% by weight), and wet/dry weight ratios are shown for each 2-cm section in Table 6.1. The water content (% by weight) is plotted in Fig. 6.4.

The moisture (105°C) and ash contents (450°C) in each section of the peat core were determined according to ASTM D 2974-87 "Standard test methods for moisture, ash, and organic matter of peat and other organic soils" (1993). The % moisture contents (calculated by 100 times the weight loss on drying at 105°C divided by the air-dried weight of peat), and ash contents (expressed relative to the dry weight at 105°C) are listed in Table 6.2. The ash content is plotted in Fig. 6.5.

Table 6.1 Section wet and dry weights of a Flanders Moss peat core collected on 11/9/01.

Sample depth (cm)	Wet weight (g)	Air-dried weight (g)	Wet/dry weight ratio	Water content by weight (%)
0-2	50.194	4.072	12.327	91.9
2-4	53.843	6.382	8.437	88.1
4-6	56.496	8.709	6.487	84.6
6-8	50.719	8.676	5.846	82.9
8-10	53.240	8.369	6.362	84.3
10-12	45.103	6.856	6.579	84.8
12-14	55.171	8.011	6.887	85.5
14-16	52.381	6.485	8.077	87.6
16-18	52.847	6.302	8.386	88.1
18-20	55.129	5.571	9.896	89.9
20-22	48.057	4.343	11.065	91.0
22-24	48.776	4.379	11.139	91.0
24-26	48.978	4.096	11.958	91.6
26-28	51.565	4.529	11.386	91.2
28-30	56.028	4.882	11.476	91.3
30-32	49.808	4.594	10.842	90.8
32-34	48.747	4.812	10.130	90.1
34-36	57.306	4.665	12.284	91.9
36-38	51.089	3.926	13.013	92.3
38-40	53.081	3.810	13.932	92.8
40-42	52.997	4.098	12.932	92.3
42-44	43.536	3.306	13.169	92.4
44-46	47.747	3.452	13.832	92.8
46-48	55.304	4.060	13.622	92.7
48-50	42.252	2.760	15.309	93.5
50-52	55.392	3.680	15.052	93.4
52-54	48.299	3.389	14.252	93.0
54-56	61.412	4.814	12.757	92.2
56-58	46.157	3.358	13.745	92.7
58-60	52.413	3.582	14.632	93.2
60-62	52.805	3.764	14.029	92.9
62-64	53.564	4.028	13.298	92.5
64-66	53.241	4.265	12.483	92.0
66-68	51.193	4.179	12.250	91.8
68-70	48.794	4.189	11.648	91.4
70-72	53.821	4.336	12.413	91.9
72-74	48.225	4.037	11.946	91.6
74-76	53.626	4.715	11.373	91.2
76-78	53.208	4.454	11.946	91.6
78-80	49.520	4.413	11.221	91.1
80-82	52.375	4.965	10.549	90.5
82-84	50.053	4.540	11.025	90.9
84-86	52.060	4.059	12.826	92.2
86-88	48.751	3.246	15.019	93.3
88-90	54.216	3.908	13.873	92.8
90-92	48.056	4.532	10.604	90.6
92-94	49.761	4.482	11.102	91.0
94-96	48.611	3.968	12.251	91.8

Table 6.2 Section moisture contents (calculated by 100 times the weight loss on drying at 105°C divided by the air-dried weight of peat) and ash contents (expressed relative to the dry weight at 105°C), determined in triplicate according to ASTM D 2974 - 87, in a Flanders Moss peat core collected on 11/9/01.

Depth (cm)	Moisture content (%)			Ash content (%)		
	%Moisture	±	SD (n = 3)	%Ash	±	SD (n = 3)
0-2	12.9	±	0.2	2.25	±	1.08
2-4	13.1	±	0.2	2.86	±	0.44
4-6	11.8	±	0.2	5.28	±	0.45
6-8	12.6	±	0.3	6.56	±	0.25
8-10	12.9	±	0.3	5.22	±	0.07
10-12	12.4	±	0.3	3.41	±	0.34
12-14	12.4	±	0.3	2.28	±	0.67
14-16	12.4	±	0.5	1.97	±	0.65
16-18	10.6	±	0.4	2.00	±	0.04
18-20	11.5	±	0.3	1.45	±	0.23
20-22	11.6	±	0.3	1.49	±	0.63
22-24	12.5	±	0.3	1.46	±	0.23
24-26	12.1	±	0.3	1.34	±	0.24
26-28	10.7	±	0.3	1.04	±	0.21
28-30	11.3	±	0.4	1.33	±	0.46
30-32	11.2	±	0.7	1.61	±	0.80
32-34	10.8	±	0.7	1.75	±	0.22
34-36	11.1	±	0.9	1.07	±	0.23
36-38	11.2	±	0.3	1.29	±	0.05
38-40	11.5	±	0.6	1.63	±	0.36
40-42	10.5	±	0.3	2.24	±	0.25
42-44	9.2	±	0.3	1.02	±	0.82
44-46	9.3	±	0.1	0.86	±	0.15
46-48	9.6	±	0.3	1.12	±	0.57
48-50	10.5	±	0.1	3.21	±	0.21
50-52	9.7	±	0.1	1.62	±	0.25
52-54	10.5	±	1.8	0.79	±	0.61
54-56	9.9	±	0.5	0.85	±	0.40
56-58	9.4	±	0.1	1.50	±	0.41
58-60	9.1	±	0.1	1.37	±	0.01
60-62	9.3	±	0.1	1.57	±	0.27
62-64	9.2	±	0.3	1.43	±	0.30
64-66	10.7	±	0.2	1.12	±	0.25
66-68	9.4	±	0.5	0.75	±	0.26
68-70	10.1	±	0.3	0.99	±	0.49
70-72	9.6	±	0.4	1.14	±	0.24
72-74	7.8	±	0.4	2.89	±	0.37
74-76	8.1	±	0.1	2.55	±	0.45
76-78	7.6	±	0.1	1.69	±	0.40
78-80	7.8	±	0.0	1.36	±	0.23
80-82	8.4	±	0.1	0.95	±	0.22
82-84	8.0	±	0.8	0.96	±	0.21
84-86	7.6	±	0.2	1.10	±	0.24
86-88	8.6	±	0.1	1.57	±	0.47
88-90	7.3	±	0.1	0.97	±	0.49
90-92	7.4	±	0.4	0.68	±	0.23
92-94	7.2	±	0.2	0.70	±	0.25
94-96	6.8	±	0.1	0.57	±	0.67

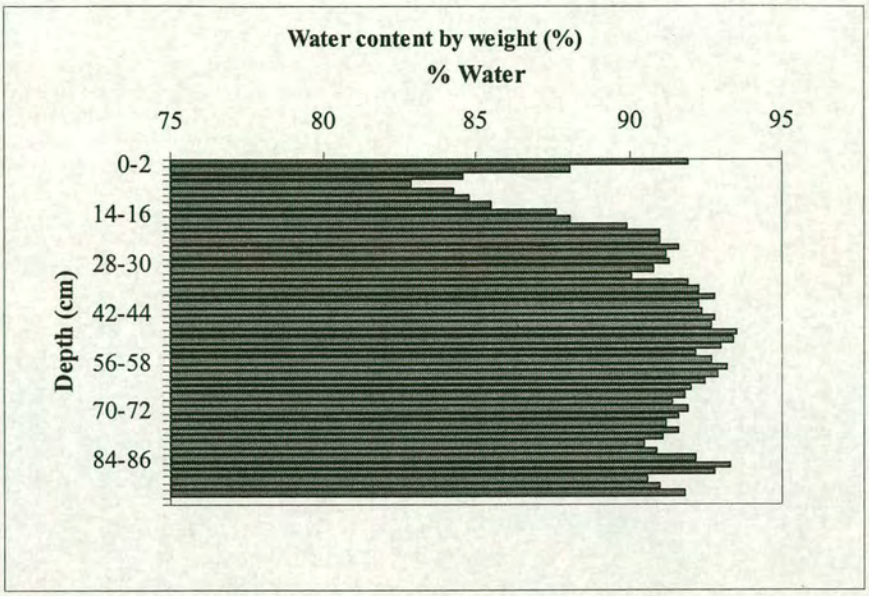


Figure 6.4 Vertical profile of water content (% by weight) of the Flanders Moss peat core collected on 11/09/2001.

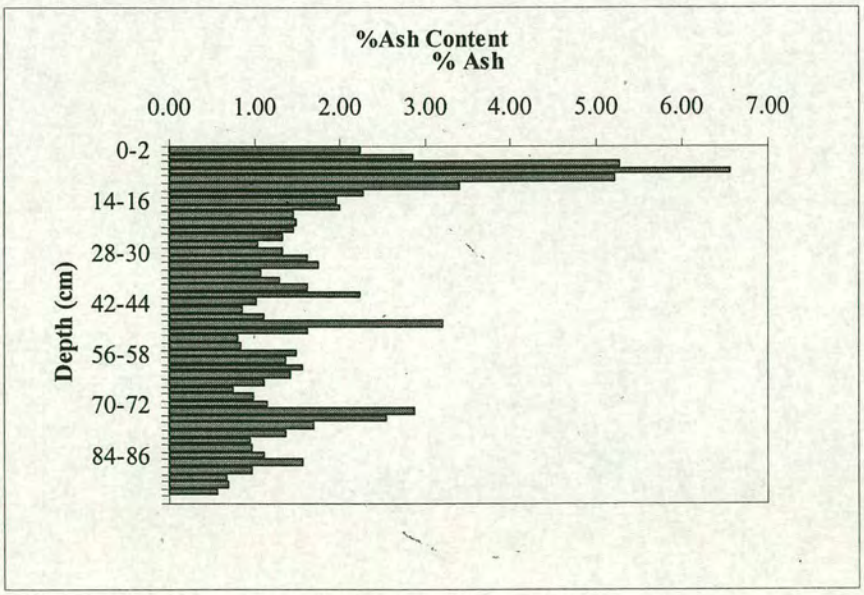


Figure 6.5 Vertical profile of ash content (% of dry weight at 105°C) of the Flanders Moss peat core collected on 11/09/2001.

6.4 Chemical pre-treatment and elemental analysis of the 2001 peat core samples

The powdered peat material was homogenised by shaking before sub-sampling. Three portions were sub-sampled from each section of peat core and digested in the microwave digestion system. Two digestion procedure protocols obtained from previous experiments (Section 3.2 of Chapter 3), the "Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat (total-recoverable digestion method)" and the "Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat (total-total digestion method)", were used for sample preparation.

6.4.1 Adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat (total-recoverable digestion method)

Approximately 0.250 g of dried ombrotrophic peat sample was accurately weighed out (three replicate samples from each section). The NIMT/UOE/FM/001 ombrotrophic peat reference material was analysed for quality control purposes in each analysis batch. These samples were placed in Pyrex beakers in a muffle furnace for four hours at 100°C, and for a further four hours at 450°C. After cooling, each sample was placed in a Teflon microwave digestion vessel with 10 ml ARISTAR HNO_3 and then digested in a CEM MARS 5 microwave digestion system. The programme used had the following features: Temperature control, Maximum power 1200 W, 100%, Phase 1-ramp to 165°C, 3.0 mins, Phase 2-ramp to 175°C, 2.5 mins, hold at 175°C 10 mins. Upon cooling, the samples were filtered through Whatman No. 542 filter paper to remove any remaining solid material. The solutions were evaporated down to approximately 1 ml on a hotplate and then made up to 25 ml in volumetric flasks with 2% v/v ARISTAR HNO_3. The sample solutions were stored in Sterilin tubes and finally analysed for Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, P, Pb, S, Ti, V, and Zn by ICP-OES. As, Cd, and Pb (in some samples) were determined by ICP-MS.

6.4.2 Adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat (total-total digestion method)

Approximately 0.250 g of dried ombrotrophic peat sample was accurately weighed out (three replicate samples from each section). The NIMT/UOE/FM/001 ombrotrophic peat reference material was analysed for quality control purposes in each analysis batch. These samples were placed in Pyrex beakers in a muffle furnace for four hours at 100°C, and for a further four hours at 450°C. After cooling, each sample was placed in a Teflon microwave digestion vessel with 9 ml ARISTAR HNO_3, 0.5 ml of ARISTAR HF, and then digested in a CEM MARS 5 microwave digestion system. The programme used had the following features: Temperature control, Maximum power 1200 W, 100%, Phase 1-ramp to 175°C, 3.0 mins, Phase 2-ramp to 180°C, 2.5 mins, hold at 180°C 9.5 mins. Upon cooling, the samples were transferred to 100 ml Teflon beakers. The solutions were evaporated down to approximately 1 ml on a hotplate and then made up to 25 ml in volumetric flasks with 2% v/v ARISTAR HNO_3. The sample solutions were stored in Sterilin tubes and finally analysed for Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, P, Pb, S, Ti, V, and Zn by ICP-OES. As, Cd, and Pb (in some samples) were determined by ICP-MS.

6.4.3 Determination of inorganic elements in the peat samples by ICP-OES and ICP-MS

The determination of elemental concentrations in the digested peat samples by ICP-OES was carried out using the Thermo Jarrell Ash IRIS instrument. Summarised instrumental conditions, analytical lines and estimated detection limits, are given in Section 3.1.1.5 of Chapter 3. These conditions and analytical lines were used throughout this research project. Details of standard solutions used for calibration were given in Section 3.1.4.3 of Chapter 3. Where concentrations were below the detection limit of ICP-OES, ICP-MS was employed using external calibration, e.g. for the total concentration of As and Cd (one replicate sample only).

6.5 Determination of isotope ratios for Pb by ICP-MS

The sections of Flanders Moss peat core collected on 11/09/01 were also investigated for Pb isotopic composition. Upon completion of elemental concentration determination, digested peat samples were analysed for stable Pb isotopes by

ICP-MS. Two replicate samples from each section were analysed. If the results from the first two were not in good agreement, a third replicate sample was then analysed. Sample solutions were diluted to the appropriate concentration range and analysed for Pb isotopes, ^{206}Pb, ^{207}Pb, ^{208}Pb using the VG PlasmaQuad3 instrument. The National Institute of Science and Technology (NIST) common Pb isotopic standard SRM981 was used throughout for calibration and mass bias correction. The parameters for set up of the instrument are shown in Table 6.3.

Table 6.3 Instrument operating conditions for ICP-MS analysis.

Mode	Pulse counting
Dwell time	2.0 ms
Reflected power	1-3 W
Mass range	203.6-209.4 amu.
Argon flow	0.75-0.84 l/min
Uptake rate	0.55 ml/min
Replicates	5
Rinse time	30 sec between each sample
Settle time	30 sec
Uptake time	150 sec
Acquisition time	60 sec

6.6 Quality assurance

The ombrotrophic peat bog reference material NIMT/UOE/FM/001 was used as a quality control in every batch of analyses for elemental concentrations in the peat core samples. Figs. 6.6 and 6.7 display quality control charts for the determination of concentrations of some elements by acid-extractable and total digestion methods, respectively. Table 6.4 shows $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$, and $^{208}Pb/^{207}Pb$ isotopic ratios in the reference material NIMT/UOE/FM/001 as determined for quality control purposes. Both the acid-extractable and total elemental concentrations obtained were close to the certified values (Table 4.10, Chapter 4). It can be seen from Figs. 6.6 and 6.7 that, during this period of analysis, elemental concentrations were generally consistent.

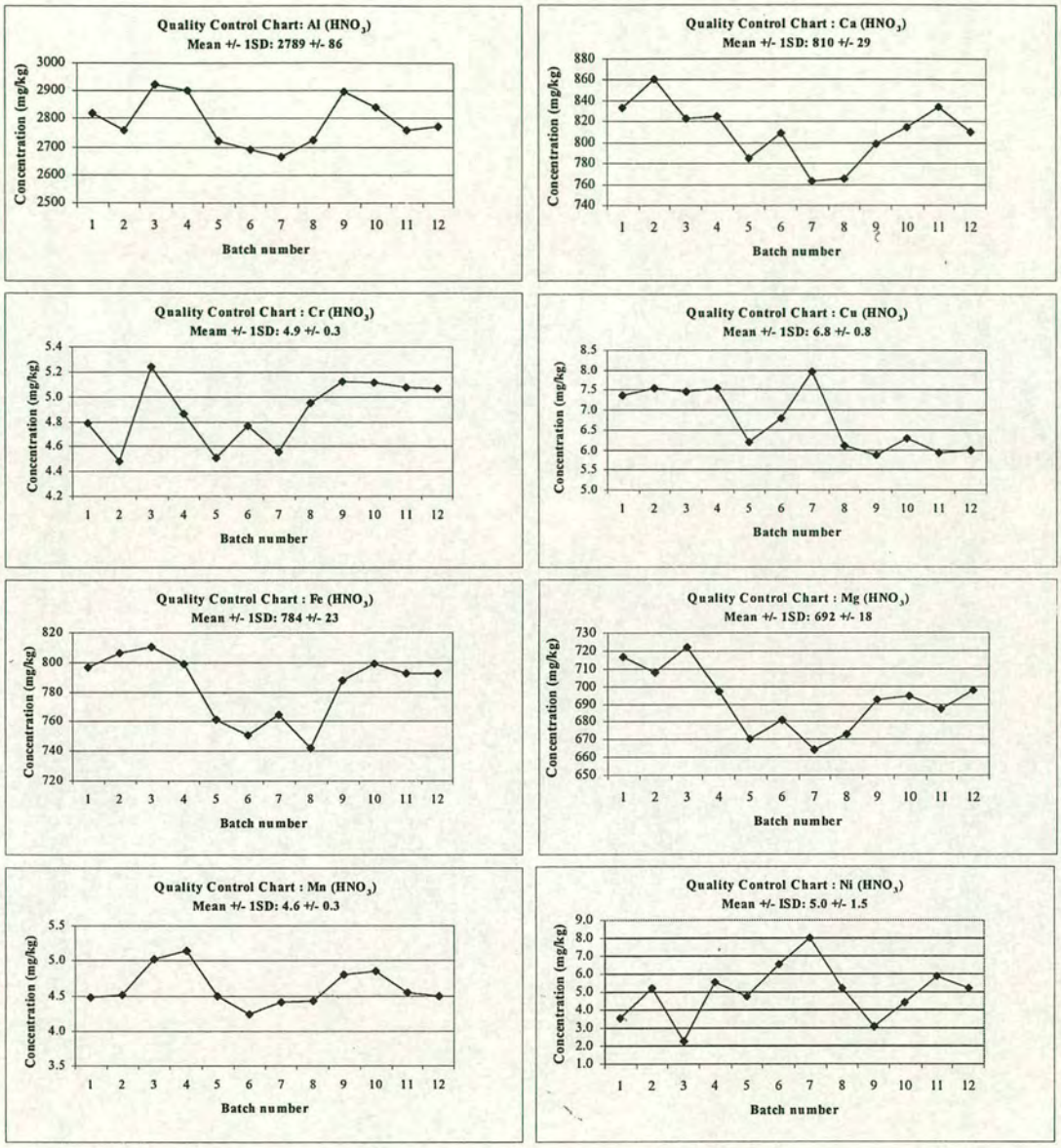


Figure 6.6 Quality control charts for some selected elements in the determination of acid-extractable elemental concentrations in the peat reference material NIMT/UOE/FM/001 during the analysis of the Flanders Moss peat core collected on 11/09/2001.

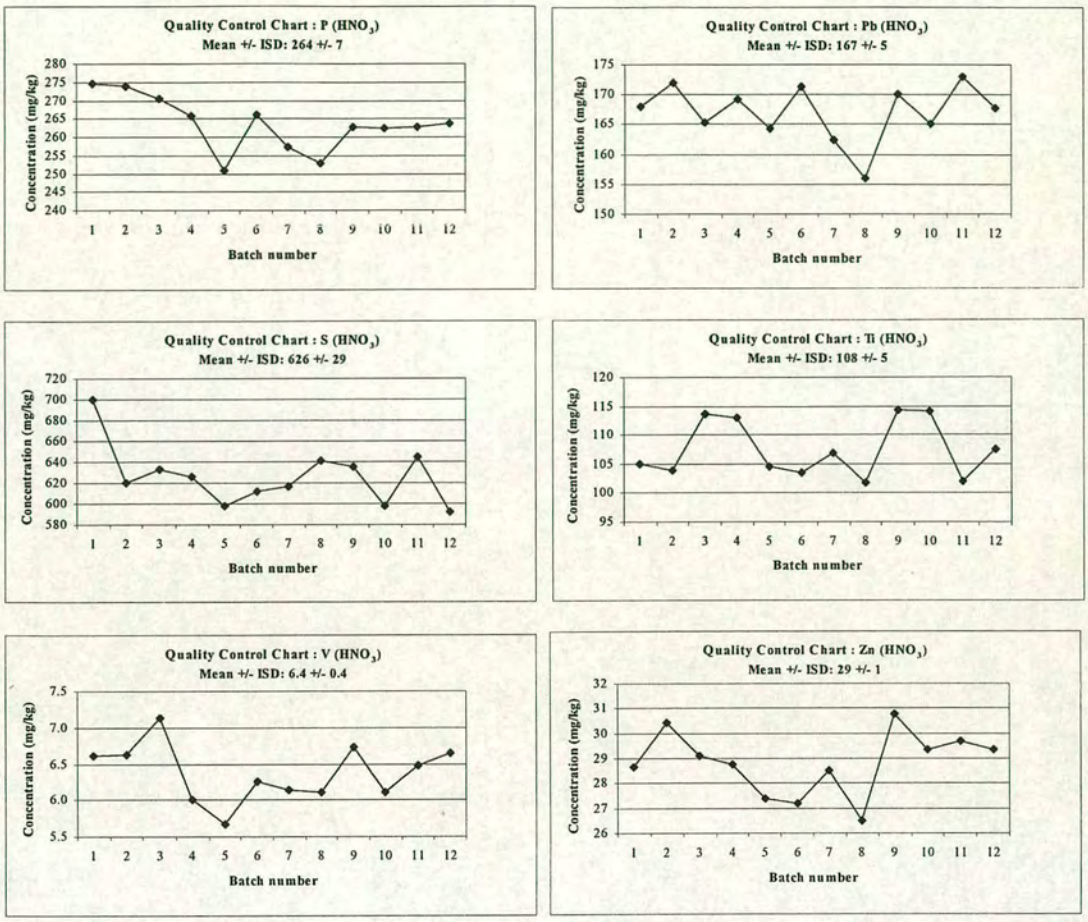


Figure 6.6 (continued) Quality control charts for some selected elements in the determination of acid-extractable elemental concentrations in the peat reference material NIMT/UOE/FM/001 during the analysis of the Flanders Moss peat core collected on 11/09/2001.

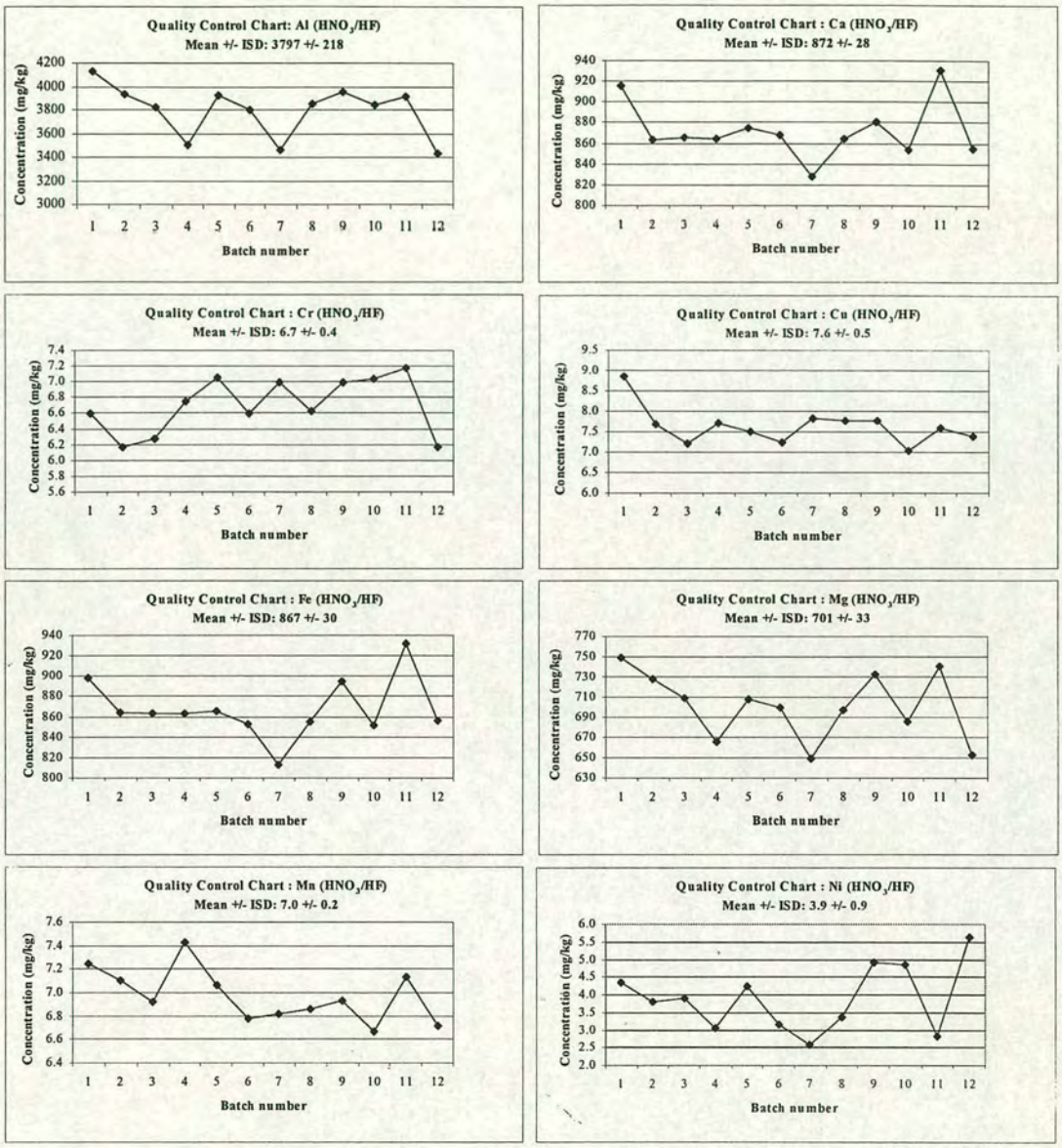


Figure 6.7 Quality control charts for some selected elements in the determination of total elemental concentrations in the peat reference material NIMT/UOE/FM/001 during the analysis of the Flanders Moss peat core collected on 11/09/2001.

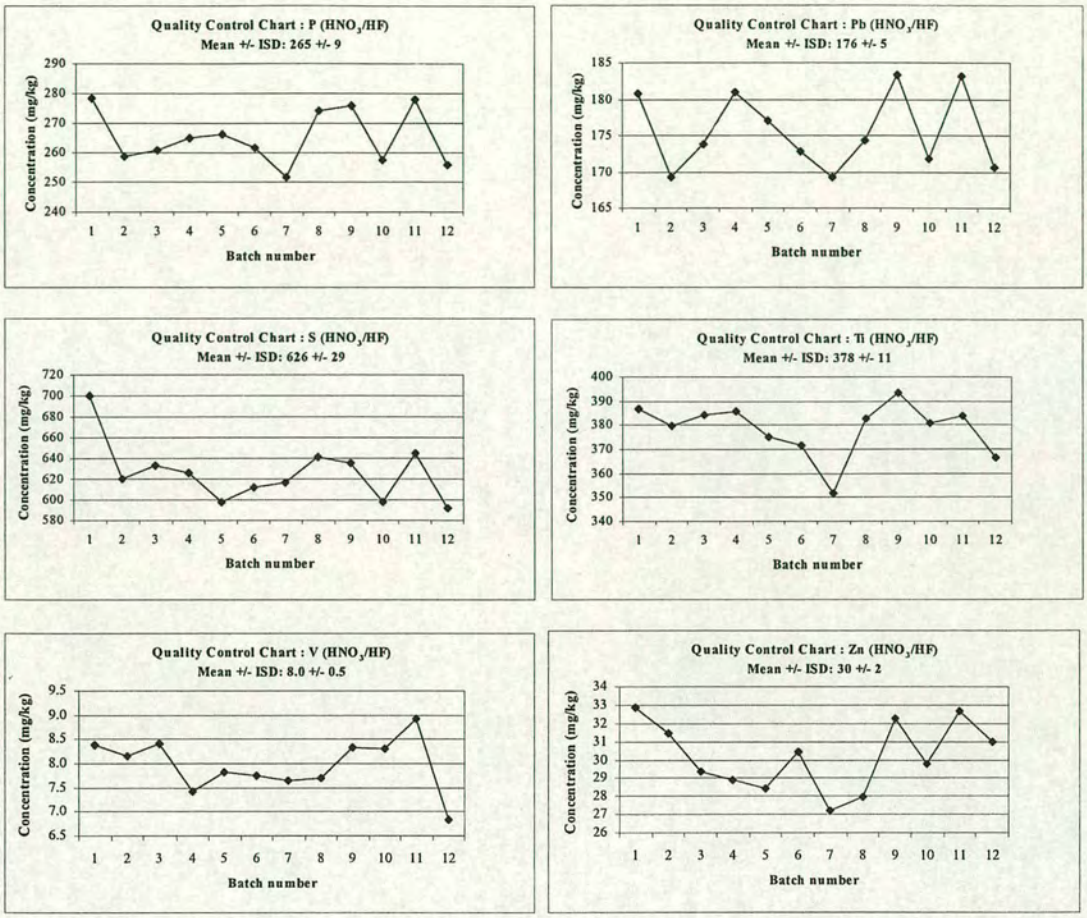


Figure 6.7 (continued) Quality control charts for some selected elements in the determination of total elemental concentrations in the peat reference material NIMT/UOE/FM/001 during the analysis of the Flanders Moss peat core collected on 11/09/2001.

Table 6.4 $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$, and $^{208}Pb/^{207}Pb$ isotopic ratios in the reference material NIMT/UOE/FM/001 as determined for quality control purposes.

Batch number	Isotopic ratios		
	$^{206}Pb/^{207}Pb \pm 1SD.$	$^{208}Pb/^{206}Pb \pm 1SD.$	$^{208}Pb/^{207}Pb \pm 1SD.$
1	1.176 ± 0.0014	2.092 ± 0.0017	2.460 ± 0.0018
2	1.177 ± 0.0012	2.092 ± 0.0036	2.462 ± 0.0024
3	1.177 ± 0.0013	2.091 ± 0.0027	2.461 ± 0.0027
4	1.176 ± 0.0010	2.088 ± 0.0027	2.455 ± 0.0016
5	1.177 ± 0.0015	2.092 ± 0.0017	2.462 ± 0.0036
6	1.178 ± 0.0006	2.093 ± 0.0041	2.466 ± 0.0049
7	1.177 ± 0.0016	2.091 ± 0.0015	2.461 ± 0.0032
8	1.176 ± 0.0013	2.093 ± 0.0028	2.461 ± 0.0032
9	1.177 ± 0.0012	2.093 ± 0.0037	2.463 ± 0.0023
10	1.177 ± 0.0008	2.094 ± 0.0029	2.465 ± 0.0036
11	1.176 ± 0.0010	2.096 ± 0.0024	2.465 ± 0.0039
12	1.175 ± 0.0011	2.095 ± 0.0017	2.462 ± 0.0022

6.7 Determination of radionuclides

Analyses for ^{210}Pb, ^{226}Ra and ^{137}Cs were performed by gamma spectrometry using a Canberra low background planar LEGe (Low Energy Ge) gamma photon detector (MacKenzie *et al.*, 1997, 1998). Sample weights of 1 or 2 g of dried, ground material were used depending upon the amount available at different depths in the core. Samples were sealed in polycarbonate containers and stored for a minimum of three weeks before analysis in order to allow ^{222}Rn to come to radioactive equilibrium with ^{226}Ra. The sample containers were positioned in a holder, which ensured reproducible geometry, on the end face of the detector for analysis. Detection efficiencies were determined for each counting geometry using standards prepared by spiking appropriate weights of peat, which had non-detectable activities of the nuclides of interest, with known activities of ^{210}Pb, ^{226}Ra and ^{137}Cs using certified standard solutions (Amersham plc). The standards were then prepared in the same geometry as the samples.

6.8 Results

6.8.1 Elemental concentrations

Elemental concentrations in the Flanders Moss peat core collected on 11/09/01 are listed in Tables 6.5 – 6.8 (acid-extractable) and Tables 6.9 – 6.13 (total). Concentrations are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat. Confidence intervals are given at 95% level for n = 3. Vertical profiles of acid-extractable compared with total elemental concentrations for the peat core collected on 11/09/01 are shown in Figs. 6.8 – 6.21. Vertical profiles of total concentrations of As and Cd are shown in Figs. 6.22 – 6.23.

Table 6.5 Acid-extractable Al, Ca, and Cr concentrations in the Flanders Moss peat core collected on 11/9/01 (concentrations are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat) (confidence intervals are given at 95% level for n = 3).

Depth (cm)	Elemental concentration (mg/kg)		
	Al	Ca	Cr
	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)
0-2	1742 ± 103	1336 ± 49	7.8 ± 1.4
2-4	2247 ± 233	1530 ± 43	8.7 ± 2.9
4-6	2892 ± 114	1479 ± 91	7.3 ± 1.0
6-8	3270 ± 201	1131 ± 34	6.1 ± 0.3
8-10	2597 ± 43	768 ± 41	3.9 ± 0.4
10-12	2207 ± 218	832 ± 41	3.1 ± 0.4
12-14	1885 ± 77	885 ± 53	2.5 ± 0.3
14-16	1723 ± 66	937 ± 22	2.3 ± 0.4
16-18	1601 ± 72	1070 ± 33	1.5 ± 0.1
18-20	1043 ± 11	1026 ± 25	1.3 ± 0.5
20-22	1033 ± 16	1045 ± 12	1.1 ± 0.2
22-24	1098 ± 8	1161 ± 24	1.1 ± 0.4
24-26	1046 ± 19	1154 ± 17	1.0 ± 0.2
26-28	949 ± 66	1121 ± 23	1.0 ± 0.5
28-30	734 ± 62	1016 ± 51	0.7 ± 0.6
30-32	795 ± 26	1066 ± 48	0.7 ± 0.5
32-34	819 ± 31	1017 ± 40	1.2 ± 0.6
34-36	595 ± 30	931 ± 24	1.0 ± 0.2
36-38	503 ± 36	867 ± 18	0.7 ± 0.6
38-40	389 ± 16	838 ± 20	0.4 ± 0.3
40-42	443 ± 53	859 ± 53	1.1 ± 0.7
42-44	561 ± 27	836 ± 22	0.9 ± 0.6
44-46	528 ± 48	860 ± 52	0.7 ± 0.5
46-48	445 ± 26	819 ± 35	0.9 ± 0.7
48-50	383 ± 15	867 ± 26	0.4 ± 0.3
50-52	357 ± 5	939 ± 25	0.4 ± 0.4
52-54	399 ± 14	974 ± 36	0.3 ± 0.2
54-56	505 ± 15	953 ± 2	0.5 ± 0.4
56-58	466 ± 39	897 ± 15	1.1 ± 0.4
58-60	393 ± 8	893 ± 47	0.8 ± 0.4
60-62	456 ± 13	972 ± 45	0.4 ± 0.5
62-64	427 ± 9	996 ± 26	0.6 ± 1.0
64-66	481 ± 15	1044 ± 17	1.4 ± 1.3
66-68	418 ± 27	926 ± 53	0.8 ± 0.2
68-70	480 ± 25	1029 ± 9	0.6 ± 0.2
70-72	479 ± 13	1052 ± 64	0.4 ± 0.5
72-74	516 ± 25	1101 ± 9	1.1 ± 0.4
74-76	579 ± 4	1135 ± 34	0.9 ± 0.2
76-78	565 ± 32	1180 ± 15	0.7 ± 0.9
78-80	605 ± 40	1062 ± 39	0.7 ± 0.2
80-82	627 ± 33	981 ± 21	1.3 ± 0.3
82-84	684 ± 13	762 ± 21	1.1 ± 0.3
84-86	601 ± 51	693 ± 35	0.8 ± 0.1
86-88	501 ± 21	783 ± 45	0.9 ± 0.6
88-90	509 ± 9	722 ± 11	0.7 ± 0.4
90-92	786 ± 41	626 ± 5	1.0 ± 0.6
92-94	787 ± 104	678 ± 35	0.8 ± 0.4
94-96	634 ± 2	700 ± 23	0.6 ± 0.7

Table 6.6 Acid-extractable Cu, Fe, Mg, and Mn concentrations in the Flanders Moss peat core collected on 11/9/01 (concentrations are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat) (confidence intervals are given at 95% level for n = 3).

Depth (cm)	Elemental concentration (mg/kg)			
	Cu	Fe	Mg	Mn
	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)
0-2	13.8 ± 1.0	1535 ± 42	1022 ± 18	11.4 ± 0.3
2-4	24.4 ± 1.3	1384 ± 83	1048 ± 19	7.8 ± 0.8
4-6	25.5 ± 2.1	1075 ± 15	1016 ± 19	5.9 ± 0.5
6-8	12.1 ± 0.8	804 ± 40	821 ± 35	5.5 ± 0.9
8-10	2.9 ± 0.7	556 ± 17	635 ± 26	3.4 ± 0.6
10-12	2.3 ± 1.1	585 ± 31	705 ± 31	3.5 ± 0.5
12-14	1.9 ± 1.0	581 ± 4	772 ± 30	2.8 ± 0.1
14-16	2.5 ± 1.1	602 ± 36	899 ± 28	2.8 ± 0.3
16-18	2.2 ± 0.4	659 ± 27	1020 ± 34	2.9 ± 0.2
18-20	2.3 ± 0.4	606 ± 11	1097 ± 24	1.6 ± 0.1
20-22	2.5 ± 1.0	614 ± 6	1125 ± 19	1.7 ± 0.1
22-24	2.1 ± 0.9	667 ± 12	1221 ± 16	1.9 ± 0.1
24-26	2.3 ± 2.0	669 ± 41	1241 ± 36	1.9 ± 0.8
26-28	1.8 ± 0.7	639 ± 27	1242 ± 38	1.4 ± 0.1
28-30	1.9 ± 0.4	549 ± 43	1201 ± 50	1.4 ± 0.3
30-32	2.5 ± 0.9	566 ± 12	1215 ± 43	1.3 ± 0.1
32-34	2.1 ± 1.0	523 ± 21	1166 ± 35	1.0 ± 0.1
34-36	1.7 ± 1.2	457 ± 3	1238 ± 39	1.0 ± 0.1
36-38	2.1 ± 0.7	403 ± 12	1212 ± 35	0.8 ± 0.2
38-40	1.5 ± 0.2	359 ± 11	1262 ± 22	0.5 ± 0.2
40-42	1.9 ± 0.7	358 ± 19	1232 ± 56	0.9 ± 0.1
42-44	2.7 ± 1.7	324 ± 9	1122 ± 41	1.9 ± 0.3
44-46	3.0 ± 2.0	292 ± 28	1176 ± 30	2.5 ± 0.2
46-48	2.7 ± 0.8	267 ± 17	1182 ± 37	2.4 ± 0.1
48-50	1.9 ± 0.4	254 ± 14	1272 ± 38	1.2 ± 0.3
50-52	1.5 ± 0.6	260 ± 15	1383 ± 23	1.1 ± 0.2
52-54	0.9 ± 1.4	269 ± 7	1398 ± 45	1.5 ± 0.1
54-56	1.2 ± 1.3	255 ± 3	1234 ± 25	1.2 ± 0.1
56-58	1.5 ± 1.6	250 ± 29	1193 ± 13	1.5 ± 0.1
58-60	1.0 ± 1.0	235 ± 15	1292 ± 36	1.1 ± 0.1
60-62	1.2 ± 0.5	281 ± 11	1337 ± 55	2.0 ± 0.3
62-64	1.0 ± 0.7	256 ± 10	1408 ± 22	1.2 ± 0.1
64-66	3.8 ± 1.4	285 ± 6	1429 ± 22	1.6 ± 0.1
66-68	2.3 ± 2.4	248 ± 23	1325 ± 90	2.6 ± 0.3
68-70	1.1 ± 0.5	276 ± 14	1415 ± 42	2.2 ± 0.1
70-72	0.7 ± 0.7	270 ± 18	1513 ± 51	1.7 ± 0.1
72-74	1.1 ± 0.8	288 ± 11	1518 ± 39	1.4 ± 0.1
74-76	1.4 ± 0.7	314 ± 29	1532 ± 63	1.1 ± 0.1
76-78	1.5 ± 1.4	316 ± 15	1615 ± 70	0.9 ± 0.1
78-80	1.3 ± 0.6	287 ± 16	1418 ± 65	0.8 ± 0.1
80-82	1.0 ± 0.7	256 ± 8	1246 ± 18	0.7 ± 0.1
82-84	0.9 ± 0.8	225 ± 21	1022 ± 27	0.8 ± 0.1
84-86	0.8 ± 1.1	201 ± 8	1106 ± 38	1.4 ± 0.2
86-88	0.9 ± 0.6	210 ± 12	1342 ± 62	0.8 ± 0.1
88-90	1.1 ± 0.5	185 ± 7	1212 ± 27	0.8 ± 0.1
90-92	0.5 ± 0.7	190 ± 5	940 ± 20	0.9 ± 0.1
92-94	0.5 ± 0.1	210 ± 19	1068 ± 48	0.7 ± 0.2
94-96	0.8 ± 1.0	204 ± 9	1141 ± 6	0.7 ± 0.1

Table 6.7 Acid-extractable Ni, P, and Pb concentrations in the Flanders Moss peat core collected on 11/9/01 (concentrations are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat) (confidence intervals are given at 95% level for n = 3).

Depth (cm)	Elemental concentration (mg/kg)		
	Ni	P	Pb
	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)
0-2	7.8 ± 2.9	623 ± 3	166 ± 1
2-4	11.1 ± 2.7	534 ± 7	184 ± 5
4-6	8.7 ± 1.6	351 ± 4	179 ± 9
6-8	6.3 ± 3.8	280 ± 2	139 ± 4
8-10	3.1 ± 1.0	284 ± 19	66 ± 5
10-12	3.4 ± 2.1	267 ± 18	56 ± 4
12-14	2.6 ± 2.2	254 ± 14	39 ± 4
14-16	3.8 ± 1.8	227 ± 11	26 ± 1
16-18	3.6 ± 3.0	184 ± 5	25 ± 2
18-20	4.0 ± 1.0	156 ± 1	11 ± 2
20-22	2.7 ± 1.7	138 ± 2	10 ± 4
22-24	7.4 ± 2.2	118 ± 5	11 ± 3
24-26	3.4 ± 0.7	122 ± 4	10 ± 1
26-28	1.2 ± 0.2	114 ± 2	8 ± 1
28-30	2.1 ± 3.3	105 ± 2	3 ± 3
30-32	1.5 ± 1.9	109 ± 1	4 ± 3
32-34	3.4 ± 1.1	111 ± 3	3 ± 2
34-36	5.1 ± 1.1	94 ± 5	3 ± 3
36-38	4.5 ± 3.2	88 ± 5	<2.8*
38-40	6.2 ± 3.9	69 ± 3	<2.8
40-42	9.3 ± 5.6	90 ± 7	<2.8
42-44	5.4 ± 4.7	107 ± 1	<2.8
44-46	7.6 ± 6.0	110 ± 5	<2.8
46-48	8.6 ± 1.9	101 ± 9	<2.8
48-50	5.1 ± 4.2	82 ± 5	<2.8
50-52	4.7 ± 4.6	72 ± 9	<2.8
52-54	10.7 ± 4.7	78 ± 10	<2.8
54-56	6.3 ± 3.5	104 ± 6	<2.8
56-58	11.7 ± 3.3	105 ± 2	<2.8
58-60	4.1 ± 0.5	92 ± 9	<2.8
60-62	3.3 ± 1.8	96 ± 6	<2.8
62-64	3.7 ± 1.7	97 ± 8	<2.8
64-66	21.9 ± 1.1	118 ± 1	<2.8
66-68	4.1 ± 4.0	107 ± 6	<2.8
68-70	15.4 ± 3.9	117 ± 1	<2.8
70-72	2.8 ± 3.3	112 ± 3	<2.8
72-74	1.1 ± 2.3	126 ± 1	<2.8
74-76	8.6 ± 9.0	128 ± 5	<2.8
76-78	7.5 ± 1.7	117 ± 6	<2.8
78-80	0.7 ± 1.5	125 ± 7	<2.8
80-82	6.9 ± 6.1	131 ± 8	<2.8
82-84	3.4 ± 2.2	144 ± 5	<2.8
84-86	5.4 ± 6.5	124 ± 7	<2.8
86-88	2.9 ± 5.8	112 ± 10	<2.8
88-90	4.0 ± 4.3	114 ± 8	<2.8
90-92	8.7 ± 1.1	123 ± 6	<2.8
92-94	8.9 ± 7.6	125 ± 9	<2.8
94-96	3.9 ± 2.8	131 ± 8	<2.8

* less than detection limit of ICP-OES

Table 6.8 Acid-extractable S, Ti, V, and Zn concentrations in the Flanders Moss peat core collected on 11/9/01 (concentrations are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat) (confidence intervals are given at 95% level for n = 3).

Depth (cm)	Elemental concentration (mg/kg)			
	S	Ti	V	Zn
	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)
0-2	994 ± 77	68 ± 7	12.1 ± 1.5	279 ± 3
2-4	1361 ± 11	79 ± 10	15.3 ± 2.1	229 ± 1
4-6	1268 ± 139	118 ± 9	13.4 ± 1.2	208 ± 27
6-8	867 ± 230	136 ± 16	11.1 ± 2.3	158 ± 16
8-10	534 ± 28	102 ± 13	6.5 ± 1.1	104 ± 19
10-12	627 ± 40	84 ± 15	4.5 ± 0.9	96 ± 21
12-14	569 ± 53	76 ± 8	4.2 ± 0.9	107 ± 8
14-16	663 ± 94	64 ± 1	4.1 ± 1.4	141 ± 9
16-18	804 ± 34	49 ± 3	3.1 ± 1.2	182 ± 9
18-20	871 ± 30	38 ± 2	1.9 ± 0.4	238 ± 4
20-22	885 ± 121	37 ± 2	2.1 ± 0.8	301 ± 2
22-24	1027 ± 77	35 ± 1	1.7 ± 1.4	241 ± 4
24-26	951 ± 58	36 ± 2	1.9 ± 0.4	245 ± 1
26-28	1005 ± 110	36 ± 3	1.6 ± 0.4	253 ± 6
28-30	906 ± 123	33 ± 6	1.6 ± 0.3	231 ± 16
30-32	1007 ± 153	39 ± 1	1.5 ± 0.2	235 ± 16
32-34	936 ± 55	44 ± 3	1.0 ± 0.7	245 ± 6
34-36	902 ± 140	35 ± 2	0.4 ± 0.4	235 ± 14
36-38	852 ± 69	33 ± 3	0.7 ± 0.6	228 ± 15
38-40	839 ± 69	26 ± 1	0.4 ± 0.3	208 ± 9
40-42	815 ± 29	35 ± 2	0.8 ± 0.1	213 ± 29
42-44	811 ± 93	49 ± 3	0.9 ± 0.8	295 ± 5
44-46	854 ± 144	44 ± 2	1.5 ± 0.5	242 ± 36
46-48	818 ± 77	37 ± 9	1.0 ± 0.9	307 ± 25
48-50	768 ± 36	29 ± 1	1.4 ± 0.2	194 ± 16
50-52	925 ± 82	25 ± 1	1.0 ± 0.4	322 ± 21
52-54	959 ± 51	24 ± 1	0.6 ± 0.1	244 ± 16
54-56	925 ± 44	22 ± 4	0.6 ± 0.1	266 ± 8
56-58	820 ± 15	19 ± 1	0.5 ± 0.2	311 ± 15
58-60	909 ± 70	19 ± 1	0.6 ± 0.1	307 ± 16
60-62	886 ± 100	20 ± 1	0.4 ± 0.0	351 ± 11
62-64	909 ± 45	19 ± 1	1.0 ± 0.2	289 ± 15
64-66	855 ± 36	19 ± 2	1.6 ± 0.8	279 ± 8
66-68	843 ± 39	17 ± 2	1.2 ± 0.4	289 ± 18
68-70	851 ± 50	21 ± 3	0.9 ± 0.8	232 ± 11
70-72	941 ± 75	22 ± 1	0.6 ± 0.6	305 ± 28
72-74	923 ± 10	22 ± 2	0.4 ± 0.2	225 ± 6
74-76	993 ± 21	29 ± 2	0.7 ± 0.5	192 ± 7
76-78	993 ± 93	27 ± 2	0.4 ± 0.4	285 ± 24
78-80	865 ± 98	30 ± 3	1.0 ± 0.3	241 ± 11
80-82	767 ± 20	27 ± 2	0.7 ± 0.6	176 ± 10
82-84	594 ± 60	34 ± 3	1.0 ± 0.1	196 ± 11
84-86	559 ± 125	29 ± 1	0.8 ± 0.5	248 ± 17
86-88	682 ± 83	22 ± 2	0.8 ± 0.1	274 ± 17
88-90	615 ± 70	24 ± 2	0.5 ± 0.2	204 ± 3
90-92	489 ± 68	37 ± 2	1.0 ± 0.7	157 ± 4
92-94	479 ± 24	35 ± 4	0.8 ± 1.1	206 ± 9
94-96	551 ± 76	25 ± 3	1.2 ± 0.9	213 ± 17

Table 6.9 Total Al, Ca, and Cr concentrations in the Flanders Moss peat core collected on 11/9/01 (concentrations are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat) (confidence intervals are given at 95% level for n = 3).

Depth (cm)	Elemental concentration (mg/kg)		
	Al	Ca	Cr
	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)
0-2	3925 ± 174	1437 ± 11	14.1 ± 3.0
2-4	4055 ± 162	1603 ± 71	14.4 ± 2.3
4-6	5256 ± 329	1596 ± 52	10.8 ± 0.7
6-8	5489 ± 374	1256 ± 16	9.4 ± 0.6
8-10	4088 ± 161	862 ± 29	5.8 ± 0.4
10-12	3017 ± 64	892 ± 20	4.0 ± 0.2
12-14	2403 ± 110	888 ± 50	3.0 ± 0.3
14-16	2130 ± 88	963 ± 11	2.7 ± 0.4
16-18	1729 ± 65	1076 ± 16	2.0 ± 0.2
18-20	1090 ± 12	1034 ± 9	1.3 ± 0.4
20-22	1106 ± 52	1049 ± 34	1.3 ± 0.3
22-24	1172 ± 65	1175 ± 51	1.2 ± 0.5
24-26	1161 ± 24	1138 ± 36	1.3 ± 0.6
26-28	1028 ± 20	1124 ± 18	1.1 ± 0.4
28-30	813 ± 11	1034 ± 12	0.8 ± 0.3
30-32	903 ± 26	1083 ± 21	0.8 ± 0.3
32-34	1045 ± 43	1068 ± 45	1.9 ± 0.7
34-36	679 ± 42	957 ± 19	1.4 ± 0.1
36-38	589 ± 22	908 ± 10	1.0 ± 0.5
38-40	454 ± 5	859 ± 13	0.8 ± 0.2
40-42	464 ± 46	831 ± 31	1.1 ± 0.3
42-44	652 ± 16	824 ± 29	0.9 ± 0.3
44-46	511 ± 22	775 ± 41	0.6 ± 0.2
46-48	486 ± 17	802 ± 20	0.6 ± 0.3
48-50	465 ± 10	936 ± 21	0.7 ± 0.1
50-52	419 ± 20	986 ± 41	0.6 ± 0.5
52-54	454 ± 101	982 ± 55	0.8 ± 0.3
54-56	565 ± 23	964 ± 30	0.6 ± 0.3
56-58	489 ± 42	884 ± 24	1.0 ± 0.3
58-60	457 ± 12	901 ± 20	0.9 ± 0.3
60-62	493 ± 25	972 ± 35	0.8 ± 0.2
62-64	504 ± 22	1029 ± 45	0.6 ± 0.3
64-66	553 ± 22	1045 ± 10	1.2 ± 0.6
66-68	462 ± 23	938 ± 38	1.0 ± 0.4
68-70	542 ± 32	1033 ± 40	0.9 ± 0.1
70-72	560 ± 11	1126 ± 78	1.1 ± 1.6
72-74	552 ± 13	1113 ± 30	1.2 ± 0.5
74-76	621 ± 28	1137 ± 38	1.1 ± 0.5
76-78	566 ± 34	1116 ± 48	0.8 ± 0.5
78-80	650 ± 7	1064 ± 53	1.2 ± 0.8
80-82	691 ± 30	979 ± 68	1.9 ± 0.7
82-84	769 ± 15	770 ± 29	1.8 ± 0.9
84-86	713 ± 6	703 ± 26	1.2 ± 0.4
86-88	579 ± 11	789 ± 47	1.1 ± 1.2
88-90	649 ± 32	726 ± 32	1.6 ± 0.8
90-92	1055 ± 17	657 ± 12	2.1 ± 0.6
92-94	989 ± 93	687 ± 25	1.4 ± 0.4
94-96	768 ± 47	700 ± 45	1.0 ± 0.1

Table 6.10 Total Cu, Fe, Mg, and Mn concentrations in the Flanders Moss peat core collected on 11/9/01 (concentrations are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat) (confidence intervals are given at 95% level for n = 3).

Depth (cm)	Elemental concentration (mg/kg)			
	Cu	Fe	Mg	Mn
	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)
0-2	15.2 ± 0.3	1816 ± 28	1078 ± 39	15.5 ± 0.2
2-4	26.4 ± 1.7	1565 ± 53	1099 ± 32	10.6 ± 0.4
4-6	29.4 ± 1.7	1290 ± 55	1054 ± 26	11.4 ± 1.5
6-8	16.4 ± 1.8	1010 ± 12	867 ± 31	11.2 ± 0.2
8-10	4.1 ± 0.5	692 ± 24	690 ± 24	7.1 ± 0.2
10-12	3.1 ± 1.1	782 ± 531	745 ± 7	6.6 ± 2.6
12-14	2.9 ± 2.6	612 ± 33	784 ± 19	4.3 ± 0.1
14-16	2.9 ± 0.4	657 ± 29	932 ± 5	3.8 ± 0.3
16-18	2.3 ± 0.6	677 ± 12	1033 ± 32	3.3 ± 0.2
18-20	2.1 ± 0.7	613 ± 7	1109 ± 11	1.8 ± 0.1
20-22	2.9 ± 3.0	614 ± 28	1123 ± 33	1.9 ± 0.2
22-24	2.0 ± 1.1	676 ± 41	1229 ± 61	2.1 ± 0.2
24-26	2.2 ± 0.9	669 ± 33	1238 ± 28	1.9 ± 0.1
26-28	2.5 ± 0.9	655 ± 7	1254 ± 24	1.6 ± 0.1
28-30	1.9 ± 0.6	570 ± 11	1227 ± 9	1.5 ± 0.1
30-32	2.0 ± 0.6	587 ± 16	1240 ± 42	1.6 ± 0.1
32-34	1.9 ± 0.9	575 ± 12	1222 ± 53	1.5 ± 0.1
34-36	1.1 ± 0.6	471 ± 22	1285 ± 25	1.1 ± 0.2
36-38	1.7 ± 0.2	428 ± 22	1262 ± 7	1.0 ± 0.1
38-40	1.8 ± 1.7	372 ± 4	1289 ± 16	0.7 ± 0.1
40-42	1.4 ± 0.8	345 ± 9	1219 ± 73	1.0 ± 0.2
42-44	1.6 ± 0.8	331 ± 9	1128 ± 43	2.1 ± 0.1
44-46	1.6 ± 0.6	268 ± 13	1111 ± 25	2.7 ± 0.1
46-48	1.5 ± 0.8	271 ± 11	1176 ± 49	2.4 ± 0.1
48-50	1.2 ± 0.3	288 ± 13	1370 ± 33	1.6 ± 0.1
50-52	1.2 ± 1.2	277 ± 15	1452 ± 53	1.3 ± 0.1
52-54	1.0 ± 1.4	270 ± 24	1407 ± 51	1.5 ± 0.2
54-56	1.1 ± 0.4	263 ± 16	1267 ± 43	1.4 ± 0.1
56-58	1.1 ± 0.1	234 ± 19	1211 ± 21	1.5 ± 0.1
58-60	1.0 ± 0.3	245 ± 8	1291 ± 32	1.3 ± 0.1
60-62	1.4 ± 0.7	271 ± 21	1332 ± 18	2.0 ± 0.3
62-64	1.1 ± 0.6	267 ± 7	1422 ± 54	1.4 ± 0.1
64-66	1.3 ± 0.5	294 ± 2	1463 ± 25	1.8 ± 0.1
66-68	1.1 ± 0.7	256 ± 14	1381 ± 61	2.6 ± 0.1
68-70	0.7 ± 0.8	278 ± 4	1484 ± 46	2.5 ± 0.1
70-72	1.7 ± 1.9	294 ± 8	1595 ± 25	1.9 ± 0.1
72-74	3.2 ± 0.6	292 ± 7	1515 ± 24	1.5 ± 0.1
74-76	1.2 ± 0.4	310 ± 9	1535 ± 39	1.2 ± 0.1
76-78	1.2 ± 0.9	297 ± 23	1576 ± 8	1.0 ± 0.1
78-80	1.5 ± 1.4	289 ± 7	1407 ± 25	0.8 ± 0.1
80-82	1.3 ± 0.5	259 ± 17	1244 ± 30	0.7 ± 0.1
82-84	0.7 ± 1.1	222 ± 10	1039 ± 44	1.0 ± 0.1
84-86	1.3 ± 0.7	212 ± 10	1111 ± 54	1.5 ± 0.2
86-88	0.8 ± 0.7	217 ± 15	1348 ± 50	1.0 ± 0.1
88-90	1.2 ± 0.4	205 ± 8	1241 ± 55	1.2 ± 0.2
90-92	0.8 ± 0.8	222 ± 6	1001 ± 14	1.3 ± 0.2
92-94	1.1 ± 0.9	232 ± 16	1078 ± 58	1.0 ± 0.2
94-96	1.2 ± 2.0	220 ± 11	1139 ± 67	0.8 ± 0.1

Table 6.11 Total Ni, P, and Pb concentrations in the Flanders Moss peat core collected on 11/9/01 (concentrations are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat) (confidence intervals are given at 95% level for n = 3). Pb concentrations below 36 cm were determined by ICP-MS with one replicate.

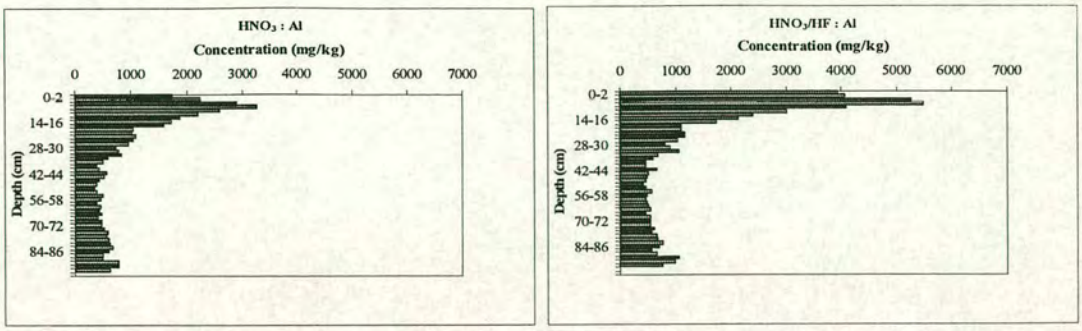
Depth (cm)	Elemental concentration (mg/kg)		
	Ni	P	Pb
	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)
0-2	11.7 ± 3.3	641 ± 31	183 ± 7
2-4	14.3 ± 1.2	546 ± 18	202 ± 10
4-6	12.0 ± 1.4	350 ± 24	193 ± 7
6-8	10.4 ± 6.0	268 ± 30	151 ± 5
8-10	4.2 ± 0.5	289 ± 17	68 ± 2
10-12	5.8 ± 3.2	261 ± 11	62 ± 5
12-14	3.9 ± 3.0	249 ± 21	36 ± 3
14-16	5.0 ± 1.6	227 ± 10	29 ± 9
16-18	2.4 ± 2.3	179 ± 6	26 ± 3
18-20	3.1 ± 3.3	147 ± 7	13 ± 5
20-22	2.7 ± 3.8	130 ± 3	12 ± 2
22-24	11.4 ± 3.8	112 ± 8	13 ± 3
24-26	3.4 ± 3.3	126 ± 2	10 ± 1
26-28	5.3 ± 4.4	116 ± 2	7 ± 2
28-30	2.4 ± 2.5	108 ± 1	3 ± 2
30-32	2.7 ± 1.7	113 ± 4	4 ± 3
32-34	4.8 ± 0.5	116 ± 5	3 ± 3
34-36	4.2 ± 0.3	97 ± 4	3 ± 2
36-38	0.8 ± 0.9	95 ± 2	1.6
38-40	0.9 ± 0.1	77 ± 4	1.3
40-42	10.9 ± 2.7	90 ± 6	1.6
42-44	3.1 ± 0.6	110 ± 3	2.2
44-46	26.6 ± 12.2	106 ± 1	1.3
46-48	1.0 ± 2.0	102 ± 4	1.0
48-50	2.1 ± 0.9	91 ± 3	1.5
50-52	0.3 ± 0.6	81 ± 3	0.8
52-54	13.5 ± 9.3	81 ± 5	0.7
54-56	0.5 ± 1.0	110 ± 16	0.8
56-58	23.3 ± 8.3	105 ± 5	1.0
58-60	1.2 ± 0.8	97 ± 1	1.0
60-62	10.3 ± 3.9	100 ± 6	0.9
62-64	0.6 ± 0.2	106 ± 4	0.6
64-66	19.4 ± 11.2	121 ± 4	0.9
66-68	3.6 ± 0.6	106 ± 6	0.7
68-70	20.9 ± 1.4	118 ± 4	0.5
70-72	1.2 ± 0.2	121 ± 4	0.7
72-74	6.5 ± 2.0	125 ± 6	1.4
74-76	0.8 ± 0.7	126 ± 2	1.3
76-78	9.9 ± 1.9	113 ± 4	1.1
78-80	1.2 ± 0.9	124 ± 4	1.7
80-82	1.2 ± 0.7	130 ± 2	3.0
82-84	4.0 ± 6.4	144 ± 11	3.3
84-86	5.6 ± 2.5	126 ± 1	3.5
86-88	0.6 ± 0.4	114 ± 7	3.6
88-90	2.7 ± 2.6	119 ± 3	4.0
90-92	3.3 ± 2.8	132 ± 3	4.2
92-94	2.8 ± 1.0	128 ± 11	3.6
94-96	2.7 ± 0.8	134 ± 5	2.9

Table 6.12 Total S, Ti, V, and Zn concentrations in the Flanders Moss peat core collected on 11/9/01 (concentrations are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat) (confidence intervals are given at 95% level for n = 3).

Depth (cm)	Elemental concentration (mg/kg)			
	S	Ti	V	Zn
	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)	Concentration +/- 95% CI (n = 3)
0-2	1036 ± 66	237 ± 26	15.9 ± 1.1	260 ± 20
2-4	1347 ± 132	235 ± 13	18.9 ± 1.3	204 ± 10
4-6	1265 ± 217	401 ± 12	17.4 ± 0.5	195 ± 36
6-8	901 ± 173	532 ± 59	14.5 ± 0.3	134 ± 9
8-10	532 ± 16	502 ± 36	8.4 ± 0.3	120 ± 15
10-12	648 ± 39	348 ± 24	5.8 ± 1.8	101 ± 3
12-14	550 ± 92	251 ± 7	4.3 ± 1.4	116 ± 20
14-16	660 ± 81	197 ± 12	5.0 ± 0.3	159 ± 9
16-18	802 ± 31	115 ± 5	3.7 ± 1.7	182 ± 8
18-20	895 ± 86	62 ± 1	2.1 ± 0.5	242 ± 5
20-22	883 ± 168	67 ± 6	1.7 ± 0.9	296 ± 8
22-24	1068 ± 71	67 ± 4	1.7 ± 1.4	244 ± 13
24-26	963 ± 71	78 ± 1	2.1 ± 0.7	241 ± 10
26-28	984 ± 113	66 ± 1	2.0 ± 0.3	256 ± 7
28-30	902 ± 144	56 ± 3	0.7 ± 0.2	239 ± 2
30-32	1019 ± 74	71 ± 2	1.6 ± 1.0	235 ± 7
32-34	932 ± 30	99 ± 4	1.9 ± 0.3	241 ± 12
34-36	966 ± 127	60 ± 6	1.0 ± 0.6	232 ± 12
36-38	890 ± 173	51 ± 1	0.9 ± 0.9	232 ± 2
38-40	878 ± 159	39 ± 1	0.8 ± 0.4	222 ± 10
40-42	780 ± 65	46 ± 1	0.9 ± 0.9	195 ± 16
42-44	807 ± 36	74 ± 3	1.4 ± 0.5	299 ± 9
44-46	772 ± 137	51 ± 2	1.6 ± 0.6	225 ± 5
46-48	808 ± 29	47 ± 2	1.1 ± 0.8	296 ± 2
48-50	877 ± 46	40 ± 1	1.5 ± 1.8	207 ± 8
50-52	998 ± 48	33 ± 3	0.9 ± 0.3	344 ± 10
52-54	938 ± 86	32 ± 4	1.0 ± 0.8	253 ± 7
54-56	908 ± 4	37 ± 1	1.5 ± 0.7	267 ± 3
56-58	798 ± 17	34 ± 2	0.9 ± 0.3	307 ± 25
58-60	882 ± 42	32 ± 2	0.8 ± 0.6	300 ± 10
60-62	885 ± 111	33 ± 1	1.0 ± 0.1	347 ± 6
62-64	951 ± 50	34 ± 2	0.8 ± 0.5	287 ± 14
64-66	895 ± 13	36 ± 1	0.9 ± 0.5	237 ± 6
66-68	862 ± 10	28 ± 2	1.0 ± 1.1	250 ± 18
68-70	894 ± 70	38 ± 4	0.5 ± 0.8	193 ± 14
70-72	952 ± 133	43 ± 1	1.2 ± 0.6	277 ± 8
72-74	905 ± 79	41 ± 2	0.9 ± 0.6	228 ± 8
74-76	975 ± 86	49 ± 2	1.3 ± 1.1	193 ± 3
76-78	965 ± 171	43 ± 1	0.5 ± 0.8	272 ± 12
78-80	860 ± 118	52 ± 1	1.7 ± 1.0	239 ± 9
80-82	785 ± 39	52 ± 3	1.1 ± 0.2	175 ± 14
82-84	598 ± 11	70 ± 2	1.2 ± 1.0	195 ± 3
84-86	539 ± 126	65 ± 2	1.6 ± 0.9	252 ± 12
86-88	703 ± 109	45 ± 1	1.1 ± 0.9	275 ± 23
88-90	662 ± 15	59 ± 3	1.1 ± 1.5	172 ± 11
90-92	513 ± 19	103 ± 4	1.6 ± 0.5	125 ± 6
92-94	500 ± 76	88 ± 6	1.2 ± 1.6	168 ± 6
94-96	565 ± 82	61 ± 5	1.2 ± 0.8	173 ± 24

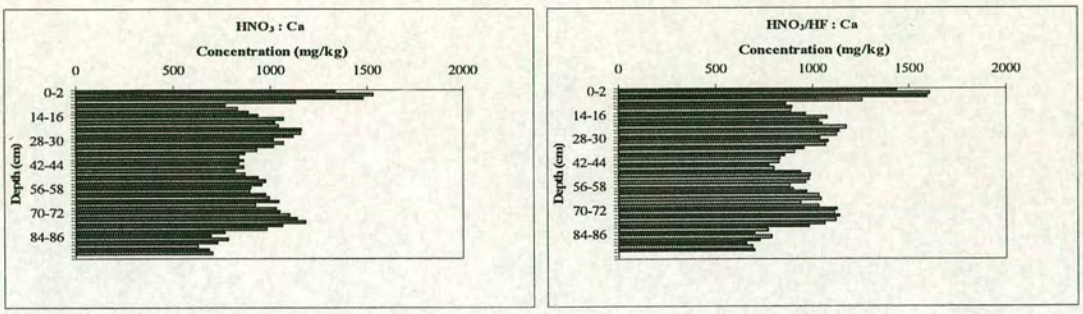
Table 6.13 Total As and Cd concentrations in the Flanders Moss peat core collected on 11/9/01 determined by ICP-MS (concentrations are expressed in mg/kg on a dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat).

Depth (cm)	Elemental concentration (mg/kg)	
	As	Cd
0-2	2.49	0.590
2-4	3.91	0.840
4-6	6.12	0.920
6-8	6.95	0.800
8-10	3.56	0.530
10-12	2.81	0.550
12-14	1.94	0.410
14-16	1.73	0.350
16-18	2.05	0.340
18-20	1.60	0.170
20-22	1.47	0.170
22-24	1.32	0.190
24-26	1.06	0.210
26-28	0.94	0.160
28-30	0.79	0.064
30-32	0.94	0.100
32-34	0.88	0.150
34-36	0.66	0.120
36-38	0.66	0.058
38-40	0.58	0.051
40-42	0.63	0.095
42-44	0.98	0.150
44-46	1.14	0.100
46-48	1.01	0.064
48-50	0.76	0.078
50-52	0.65	0.060
52-54	0.73	0.042
54-56	0.78	0.068
56-58	0.64	0.077
58-60	0.55	0.056
60-62	0.61	0.054
62-64	0.55	0.064
64-66	0.52	0.075
66-68	0.43	0.045
68-70	0.49	0.048
70-72	0.50	0.048
72-74	0.36	0.132
74-76	0.36	0.071
76-78	0.42	0.089
78-80	0.45	0.072
80-82	0.31	0.076
82-84	0.32	0.057
84-86	0.35	0.330
86-88	0.46	0.063
88-90	0.44	0.180
90-92	0.51	0.088
92-94	0.40	0.190
94-96	0.39	0.062



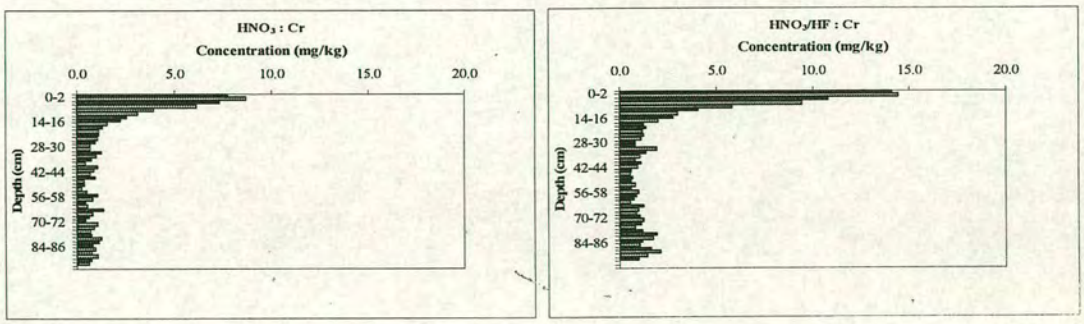
(a) (b)

Figure 6.8 Vertical profiles of (a) acid-extractable Al concentration and (b) total Al concentration for the Flanders Moss peat core collected on 11/09/01



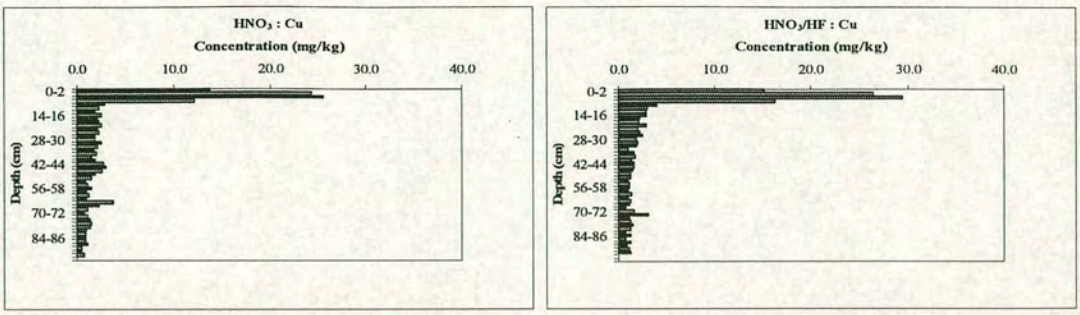
(a) (b)

Figure 6.9 Vertical profiles of (a) acid-extractable Ca concentration and (b) total Ca concentration for the Flanders Moss peat core collected on 11/09/01



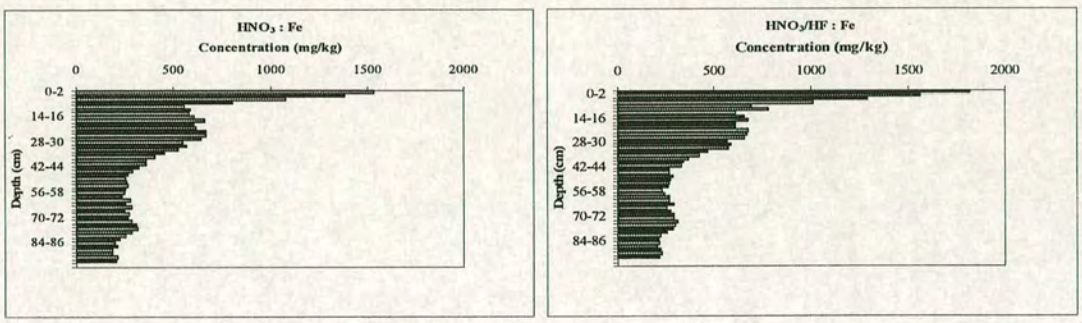
(a) (b)

Figure 6.10 Vertical profiles of (a) acid-extractable Cr concentration and (b) total Cr concentration for the Flanders Moss peat core collected on 11/09/01



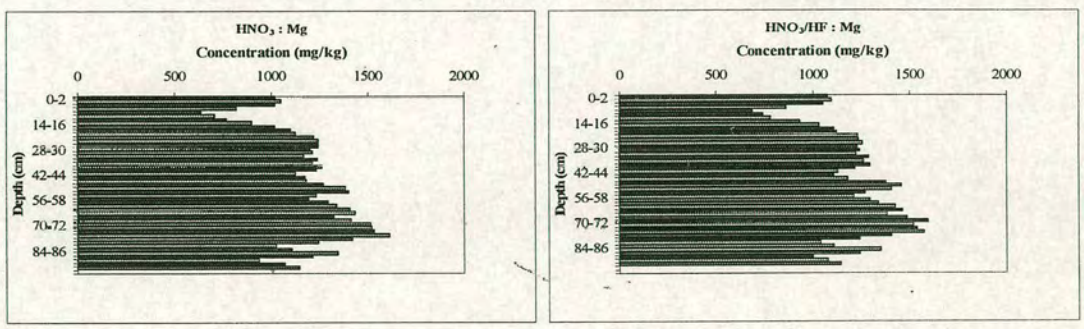
(a) (b)

Figure 6.11 Vertical profiles of (a) acid-extractable Cu concentration and (b) total Cu concentration for the Flanders Moss peat core collected on 11/09/01



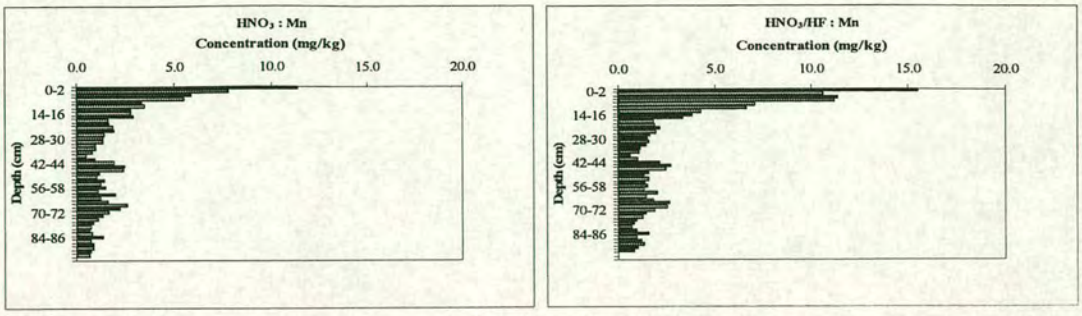
(a) (b)

Figure 6.12 Vertical profiles of (a) acid-extractable Fe concentration and (b) total Fe concentration for the Flanders Moss peat core collected on 11/09/01



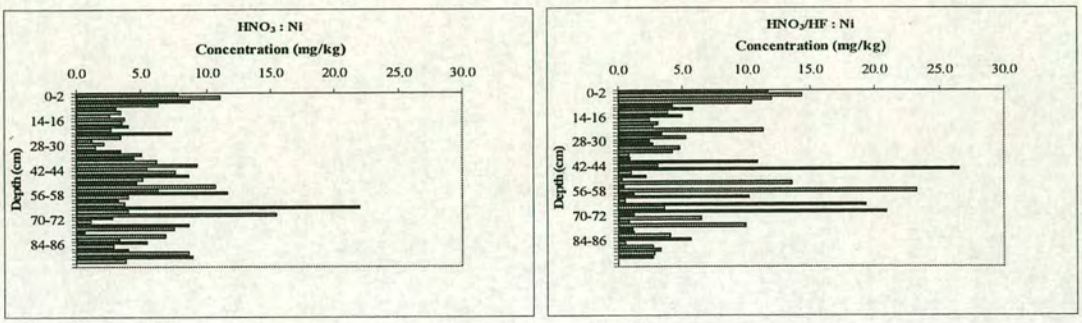
(a) (b)

Figure 6.13 Vertical profiles of (a) acid-extractable Mg concentration and (b) total Mg concentration for the Flanders Moss peat core collected on 11/09/01



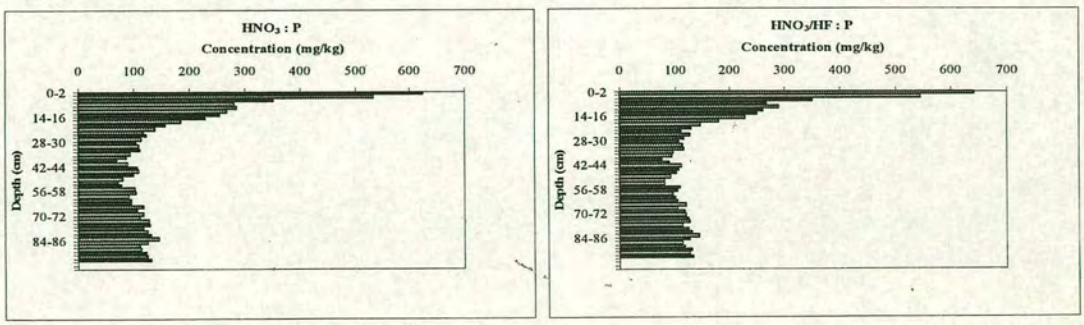
(a) (b)

Figure 6.14 Vertical profiles of (a) acid-extractable Mn concentration and (b) total Mn concentration for the Flanders Moss peat core collected on 11/09/01



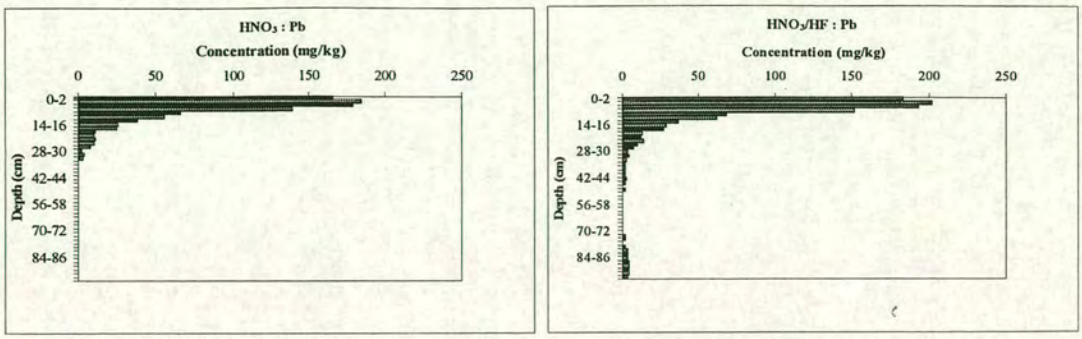
(a) (b)

Figure 6.15 Vertical profiles of (a) acid-extractable Ni concentration and (b) total Ni concentration for the Flanders Moss peat core collected on 11/09/01



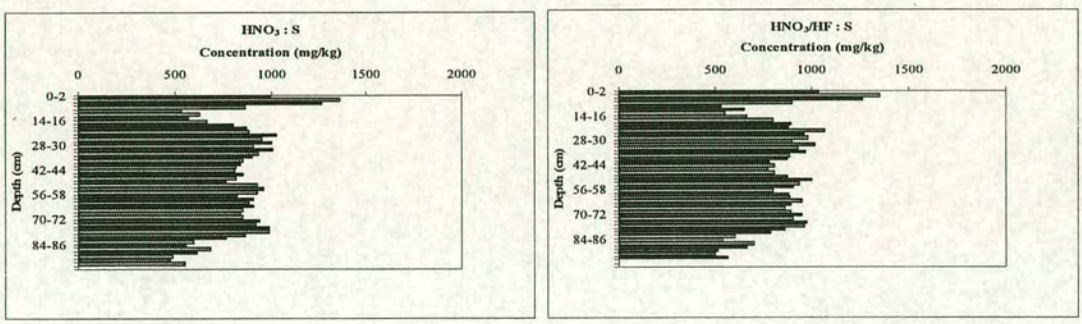
(a) (b)

Figure 6.16 Vertical profiles of (a) acid-extractable P concentration and (b) total P concentration for the Flanders Moss peat core collected on 11/09/01



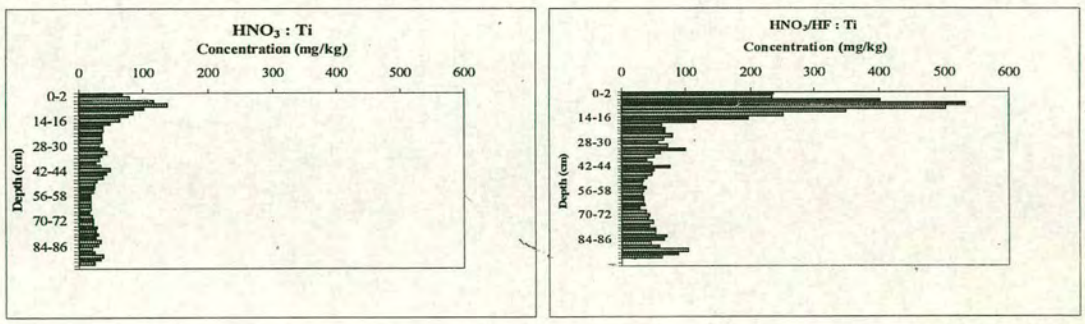
(a) (b)

Figure 6.17 Vertical profiles of (a) acid-extractable Pb concentration and (b) total Pb concentration for the Flanders Moss peat core collected on 11/09/01



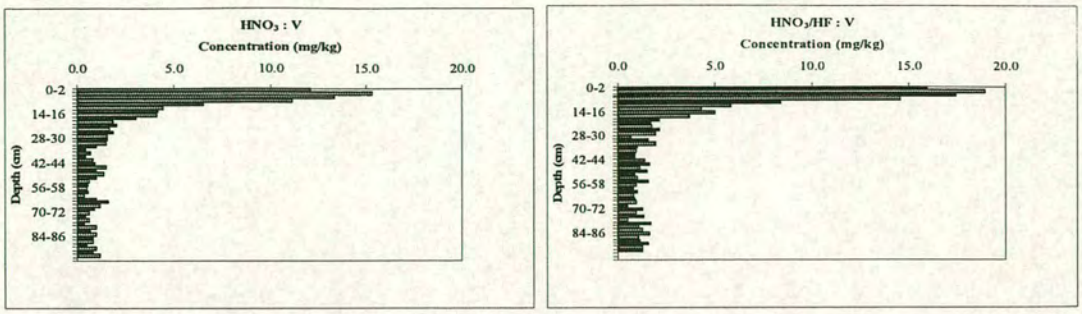
(a) (b)

Figure 6.18 Vertical profiles of (a) acid-extractable S concentration and (b) total S concentration for the Flanders Moss peat core collected on 11/09/01



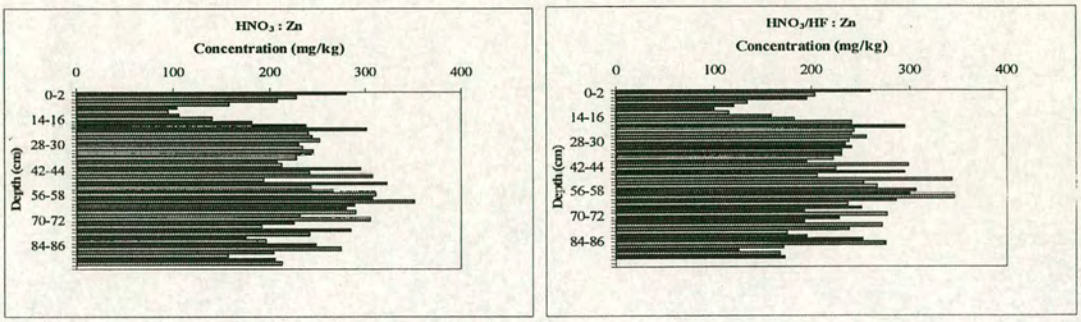
(a) (b)

Figure 6.19 Vertical profiles of (a) acid-extractable Ti concentration and (b) total Ti concentration for the Flanders Moss peat core collected on 11/09/01



(a) (b)

Figure 6.20 Vertical profiles of (a) acid-extractable V concentration and (b) total V concentration for the Flanders Moss peat core collected on 11/09/01



(a) (b)

Figure 6.21 Vertical profiles of (a) acid-extractable Zn concentration and (b) total Zn concentration for the Flanders Moss peat core collected on 11/09/01

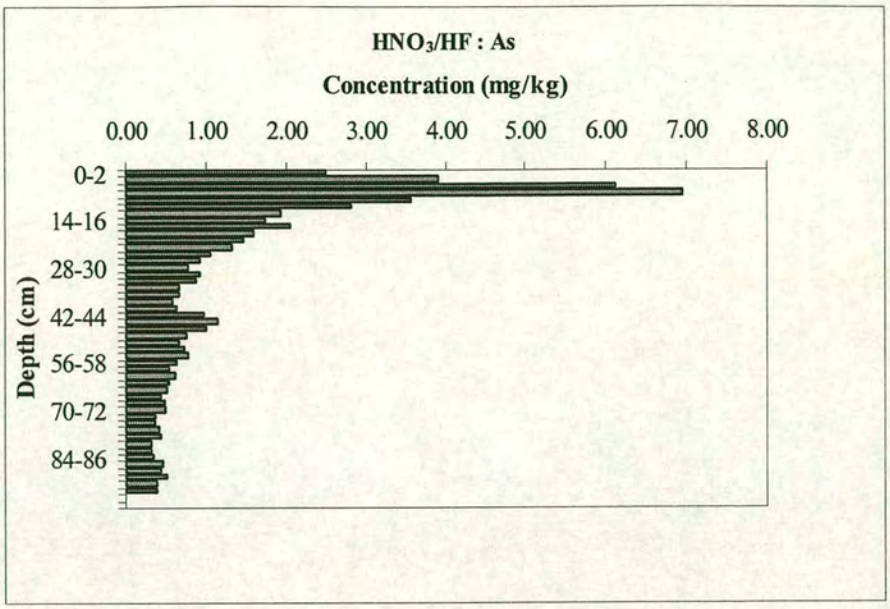


Figure 6.22: Vertical profile of total As concentration for the Flanders Moss peat core collected on 11/09/01

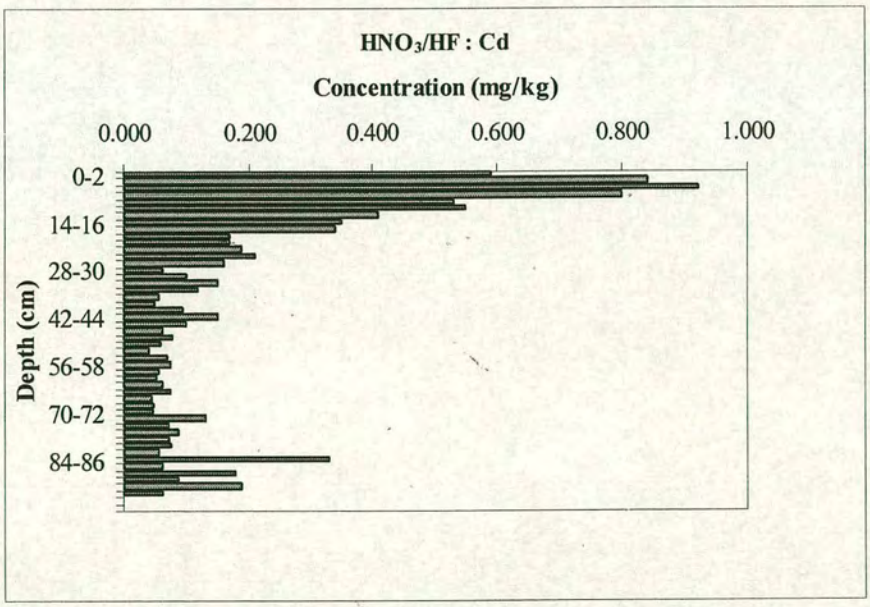


Figure 6.23: Vertical profile of total Cd concentration for the Flanders Moss peat core collected on 11/09/01

From Figs 6.8 – 6.23, it can be seen that acid-extractable and total concentration vertical profiles of inorganic elements in this Flanders Moss peat core are similar in shape and trend to each other, but total concentrations are clearly higher than acid-extractable concentrations for some major elements (i.e. Al, Fe, and Ti) and some trace elements (i.e. Cr, Ni, and V)

6.8.2 Stable Pb isotopic ratios

Table 6.14 displays $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$, and $^{208}Pb/^{207}Pb$ isotopic ratios for the individual sections of the Flanders Moss peat core collected on 11/09/01. The vertical profile of the $^{206}Pb/^{207}Pb$ ratios for this core is shown in Fig. 6.24.

Table 6.14 $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$, and $^{208}Pb/^{207}Pb$ isotopic ratios in the Flanders Moss peat core collected on 11/09/01.

Sample depth (cm)	Isotopic ratios		
	$^{206}Pb/^{207}Pb \pm 1SD.$	$^{208}Pb/^{206}Pb \pm 1SD.$	$^{208}Pb/^{207}Pb \pm 1SD.$
0-2	1.139 ± 0.0012	2.124 ± 0.0015	2.419 ± 0.0014
2-4	1.150 ± 0.0012	2.115 ± 0.0014	2.432 ± 0.0028
4-6	1.162 ± 0.0013	2.103 ± 0.0015	2.444 ± 0.0021
6-8	1.170 ± 0.0010	2.096 ± 0.0015	2.452 ± 0.0013
8-10	1.171 ± 0.0011	2.093 ± 0.0017	2.451 ± 0.0004
10-12	1.171 ± 0.0004	2.094 ± 0.0012	2.452 ± 0.0015
12-14	1.169 ± 0.0010	2.095 ± 0.0026	2.449 ± 0.0014
14-16	1.172 ± 0.0011	2.092 ± 0.0028	2.453 ± 0.0027
16-18	1.176 ± 0.0012	2.091 ± 0.0020	2.459 ± 0.0015
18-20	1.175 ± 0.0013	2.092 ± 0.0024	2.458 ± 0.0039
20-22	1.173 ± 0.0017	2.091 ± 0.0035	2.453 ± 0.0031
22-24	1.174 ± 0.0007	2.090 ± 0.0027	2.454 ± 0.0042
24-26	1.171 ± 0.0012	2.093 ± 0.0024	2.451 ± 0.0027
26-28	1.172 ± 0.0012	2.094 ± 0.0026	2.454 ± 0.0021
28-30	1.171 ± 0.0012	2.092 ± 0.0026	2.450 ± 0.0017
30-32	1.171 ± 0.0011	2.090 ± 0.0028	2.453 ± 0.0022
32-34	1.169 ± 0.0015	2.095 ± 0.0030	2.449 ± 0.0022
34-36	1.167 ± 0.0009	2.103 ± 0.0014	2.454 ± 0.0013
36-38	1.166 ± 0.0017	2.100 ± 0.0055	2.449 ± 0.0035
38-40	1.165 ± 0.0026	2.106 ± 0.0062	2.453 ± 0.0038
40-42	1.165 ± 0.0027	2.101 ± 0.0043	2.448 ± 0.0056
42-44	1.162 ± 0.0027	2.104 ± 0.0025	2.445 ± 0.0034
44-46	1.167 ± 0.0023	2.100 ± 0.0028	2.451 ± 0.0044
46-48	1.158 ± 0.0006	2.109 ± 0.0009	2.442 ± 0.0020
48-50	1.170 ± 0.0017	2.089 ± 0.0017	2.444 ± 0.0026
50-52	1.160 ± 0.0020	2.104 ± 0.0053	2.440 ± 0.0034
52-54	1.163 ± 0.0015	2.101 ± 0.0041	2.443 ± 0.0046
54-56	1.162 ± 0.0028	2.105 ± 0.0062	2.446 ± 0.0023
56-58	1.168 ± 0.0040	2.089 ± 0.0043	2.440 ± 0.0040
58-60	1.156 ± 0.0024	2.112 ± 0.0049	2.441 ± 0.0067
60-62	1.143 ± 0.0030	2.129 ± 0.0050	2.433 ± 0.0018
62-64	1.150 ± 0.0035	2.125 ± 0.0054	2.444 ± 0.0082
64-66	1.178 ± 0.0036	2.084 ± 0.0035	2.455 ± 0.0064
66-68	1.177 ± 0.0040	2.098 ± 0.0048	2.469 ± 0.0046
68-70	1.174 ± 0.0047	2.098 ± 0.0054	2.463 ± 0.0082
70-72	1.169 ± 0.0030	2.104 ± 0.0042	2.460 ± 0.0064
72-74	1.173 ± 0.0020	2.099 ± 0.0037	2.462 ± 0.0021
74-76	1.174 ± 0.0022	2.095 ± 0.0014	2.460 ± 0.0045
76-78	1.161 ± 0.0013	2.109 ± 0.0032	2.449 ± 0.0054
78-80	1.170 ± 0.0010	2.102 ± 0.0020	2.459 ± 0.0041
80-82	1.175 ± 0.0012	2.094 ± 0.0028	2.460 ± 0.0026
82-84	1.174 ± 0.0015	2.094 ± 0.0027	2.461 ± 0.0015
84-86	1.170 ± 0.0013	2.099 ± 0.0037	2.456 ± 0.0024
86-88	1.167 ± 0.0011	2.101 ± 0.0013	2.452 ± 0.0015
88-90	1.174 ± 0.0006	2.096 ± 0.0022	2.461 ± 0.0020
90-92	1.174 ± 0.0013	2.099 ± 0.0028	2.464 ± 0.0017
92-94	1.169 ± 0.0022	2.102 ± 0.0037	2.457 ± 0.0029
94-96	1.177 ± 0.0022	2.089 ± 0.0023	2.459 ± 0.0054

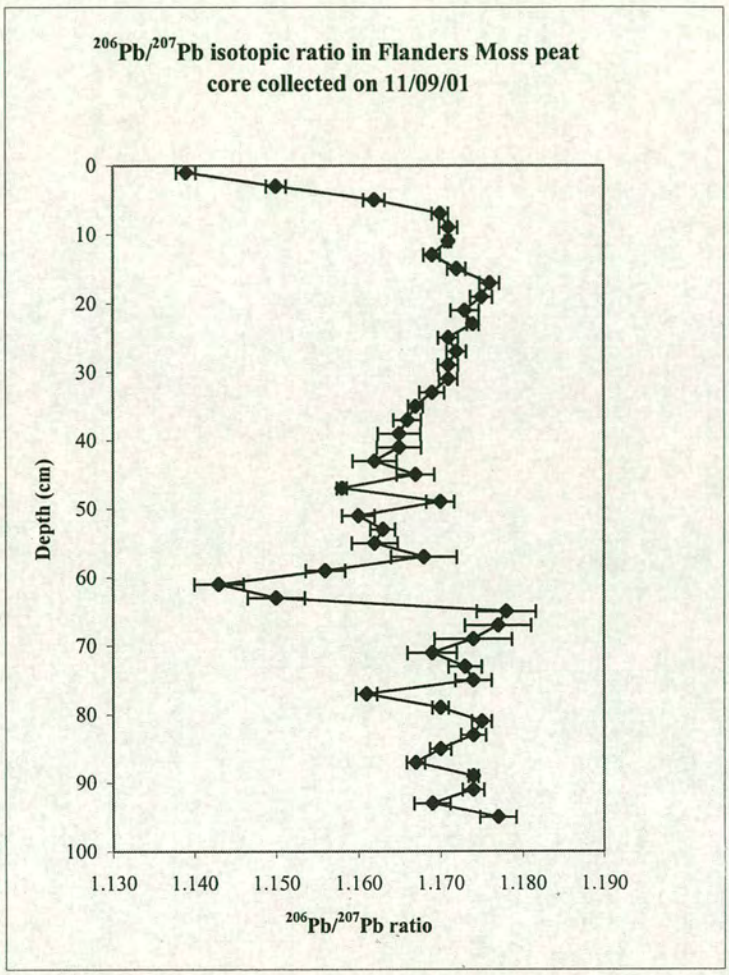


Figure 6.24: Vertical profile of the $^{206}Pb/^{207}Pb$ ratio for the Flanders Moss peat core collected on 11/09/01.

6.8.3 Radionuclides

Table 6.15 shows the results of the ^{210}Pb and ^{137}Cs specific activities (expressed in Bq kg^{-1} air-dried weight) determined in individual sections of the Flanders Moss peat core collected on 11/09/01. ^{226}Ra was not detected. The ^{210}Pb and ^{137}Cs profiles are plotted in Fig. 6.25.

Table 6.15 ^{210}Pb and ^{137}Cs specific activities in the Flanders Moss peat core collected on 11/09/01.

Section (cm)	Specific activities (Bq kg^{-1})	
	^{210}Pb	^{137}Cs
0-2	267 ± 28	421 ± 19
2-4	174 ± 24	200 ± 14
4-6	67 ± 12	96 ± 7
6-8	57 ± 10	80 ± 7
8-10	37 ± 9	124 ± 7
10-12	41 ± 15	89 ± 7
12-14	32 ± 12	73 ± 6
14-16	30 ± 13	84 ± 7
16-18	n.d.*	39 ± 5
18-20	n.d.*	52 ± 4

*n.d. = non detectable

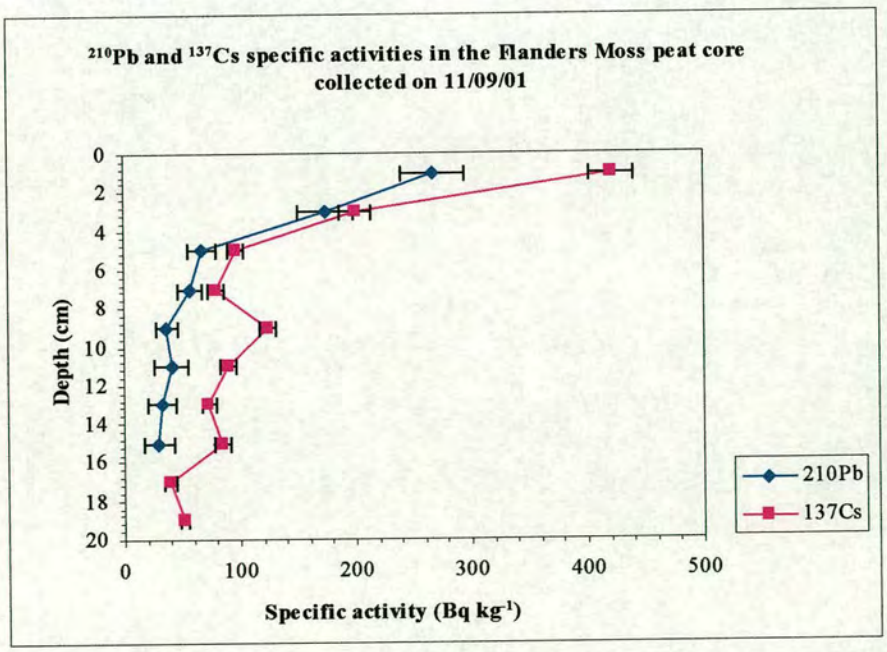


Figure 6.25 ^{210}Pb and ^{137}Cs profiles in the Flanders Moss peat core collected on 11/09/01.

6.9 Discussion

The vertical elemental concentration profiles and $^{206}Pb/^{207}Pb$ profile of the Flanders Moss peat core collected in 2001 (here designated FM01) will be discussed, including a comparison with the corresponding profiles obtained for the Flanders Moss peat monolith core collected in 1999 (here designated FM99M). Initially, the profiles (i.e. elemental profiles and $^{206}Pb/^{207}Pb$ profile) of FM01 looked entirely plausible. On closer investigation, however, doubts emerged about the top of the core, as described below.

6.9.1 ^{210}Pb dating

Using the Constant Rate of Supply (CRS) model for ^{210}Pb dating where the age of a layer i, $t_i = (1/\lambda) \times \ln (I/I_i)$, where I = total unsupported ^{210}Pb inventory in core, I_i = inventory of unsupported ^{210}Pb below layer i (Appleby and Oldfield, 1978, 1983; Oldfield and Appleby, 1985), and the ^{210}Pb data in Table 6.15, ages were obtained for the bottoms of core sections (and, by interpolation, the mid-point of each core section), as shown in Table 6.16. In addition, the corresponding $^{206}Pb/^{207}Pb$ ratios have been listed in Table 6.16.

On the basis of the ^{210}Pb dates in Table 6.16, the onset of the major shift in $^{206}Pb/^{207}Pb$ ratio to lower values, associated with the influence of imported Australian lead, appears to have occurred at least 30 years too late (i.e. the 1960s) compared with that (i.e. ca. 1930) previously established for Scotland via the analysis of peat, lake sediments and archival moss samples (Farmer *et al.*, 1996, 1997, 2002; Eades *et al.,* 2002). This result suggests that either the ^{210}Pb dating is in error or that material is somehow "missing" from the top of the core. It should be remembered that some vegetation had been removed at the time of sampling (Section 6.2).

Table 6.16 Calculated ages and dates from the ^{210}Pb dating of FM01 by the CRS method.

Depth (cm)	Age (y)	Date	Date	$^{206}Pb/^{207}Pb$
0	0	2000.7	2001	
1		1996.0	1996	1.139 ± 0.0012
2	9.4	1991.3	1992	
3		1984.6	1985	1.150 ± 0.0012
4	22.9	1977.8	1978	
5		1972.6	1973	1.162 ± 0.0013
6	33.3	1967.4	1968	
7		1961.2	1962	1.170 ± 0.0010
8	45.8	1954.9	1955	
9		1949.2	1950	1.171 ± 0.0011
10	57.2	1943.5	1944	
11		1935.8	1936	1.171 ± 0.0004
12	72.7	1928.0	1928	
13		1914.4	1915	1.169 ± 0.0010
14	99.9	1900.8	1901	
15				1.172 ± 0.0011
16				

N.B. 2000.7 means year 2000 completed plus 0.7 of a year into 2001.

The ^{210}Pb inventory of the FM01 peat core, 1.727 kBq m^{-2}, corresponds to a calculated ($-dN/dt = \lambda N$) average depositional ^{210}Pb flux of only 53.5 Bq m^{-2} y^{-1}. This is much less than (i) the theoretical value (102 ± 18 Bq m^{-2} y^{-1}) for Flanders Moss based on a typical annual rainfall of 1320 mm and the figure of 77 ± 14 Bq m^{-2} y^{-1} per metre of rainfall established for the UK by Smith *et al.* (1997), (ii) the value of 110 Bq m^{-2} y^{-1} previously obtained for a peat core from Flanders Moss (Farmer *et al.*, 1997; MacKenzie *et al.*, 1997), (iii) the value of 113 Bq m^{-2} y^{-1} obtained for a sediment core from the southern basin of Loch Lomond (Eades *et al.*, 2002) and (iv) the unpublished value of 144 ± 15 Bq m^{-2} y^{-1} obtained for a monolith core from Flanders Moss collected in 1996. Using these inventory-derived fluxes and applying a CRS-type calculation to "date" the top of the 2001 peat core, ages of 21, 23, 24 and 32 years, respectively, are obtained, yielding a mean of 25 ± 5 years. If the dates in Table 6.16 are now "corrected" by the "missing" 25

years (Table 6.17) the trend in $^{206}Pb/^{207}Pb$ is now much closer to that previously established for Scotland.

Table 6.17 Corrected ^{210}Pb ages and dates of FM01.

Depth (cm)	Age (y)	Date	Date	$^{206}Pb/^{207}Pb$
0	25	1975.7	1976	
1		1971.0	1971	1.139 ± 0.0012
2	34.4	1966.3	1967	
3		1959.6	1960	1.150 ± 0.0012
4	47.9	1952.8	1953	
5		1947.6	1948	1.162 ± 0.0013
6	58.3	1942.4	1943	
7		1936.2	1937	1.170 ± 0.0010
8	70.8	1929.9	1930	
9		1924.2	1925	1.171 ± 0.0011
10	82.2	1918.5	1919	
11		1910.8	1911	1.171 ± 0.0004
12	97.7	1903.0	1903	
13		1889.4	1890	1.169 ± 0.0010
14	124.9	1875.8	1876	
15				1.172 ± 0.0011
16				

This first, ^{210}Pb-based, evidence for the absence of some material from the top of FM01 is greatly strengthened when the $^{206}Pb/^{207}Pb$ and the elemental profiles of the FM01 and FM99M cores are compared (Section 6.9.2).

6.9.2 Comparison of FM01 and FM99M profiles

When the $^{206}Pb/^{207}Pb$ profile for the uppermost part (0 – 32 cm) of the FM01 core is plotted against the corresponding profile (0 - 43 cm, data in Table 1, Appendix G) for the FM99M core (Fig. 6.26), it is found, on the basis of the best match, that there appears to be an ~21 cm offset between the cores, i.e. 0 cm in the FM01 core corresponds to 21 cm in the FM99M core. Thus the suggestion of missing material from the top of the FM01 core (Section 6.9.1) is confirmed here.

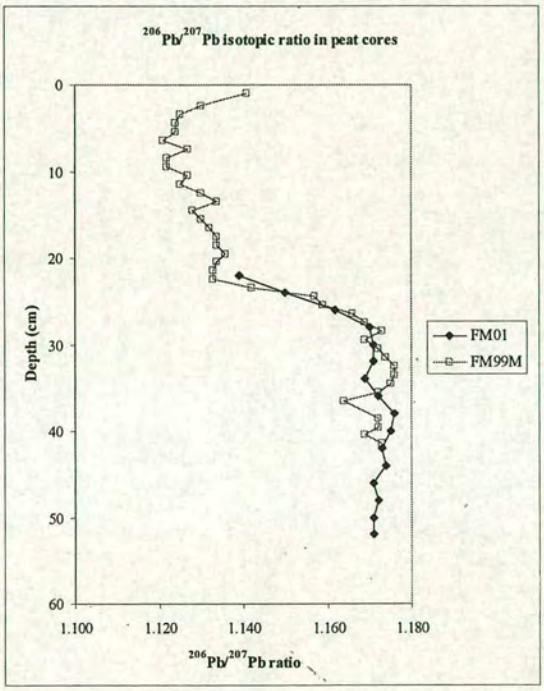


Figure 6.26 The best match of the $^{206}Pb/^{207}Pb$ ratio depth profiles in FM01 and FM99M, showing a 21 cm offset between the cores.

Furthermore, when all the profiles (including elemental concentration, ash and water content etc.) are similarly plotted with a 21 cm offset between FM99M and FM01, there is reasonably good agreement (Figs 6.27 - 6.41), i.e. 0 – 22 cm in FM01 corresponds to 21 – 43 cm in FM99M. This provides even more evidence to support the suggestion that material is missing from the top of the FM01 core.

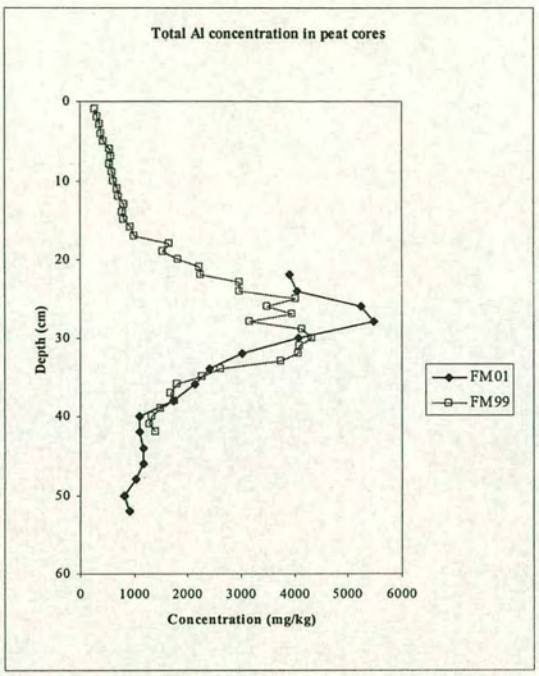


Figure 6.27 Depth profiles of Al concentration in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

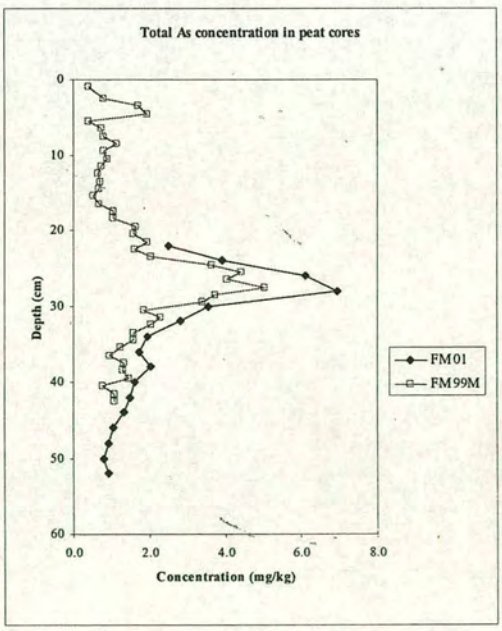


Figure 6.28 Depth profiles of As concentration in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

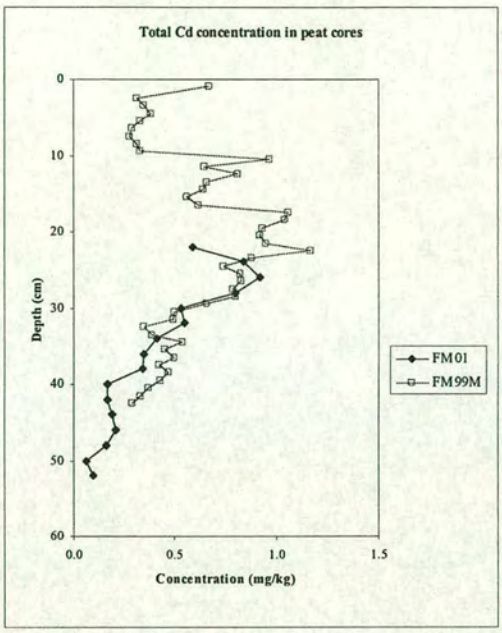


Figure 6.29 Depth profiles of Cd concentration in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

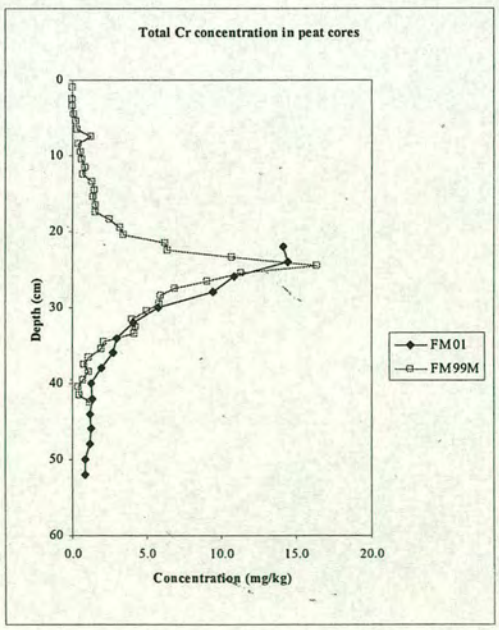


Figure 6.30 Depth profiles of Cr concentration in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

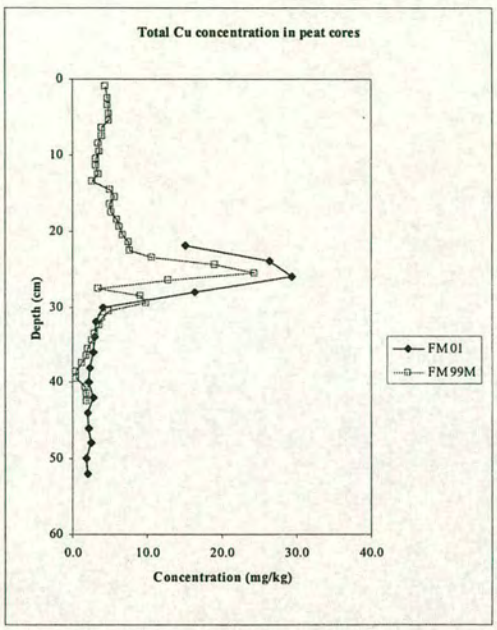


Figure 6.31 Depth profiles of Cu concentration in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

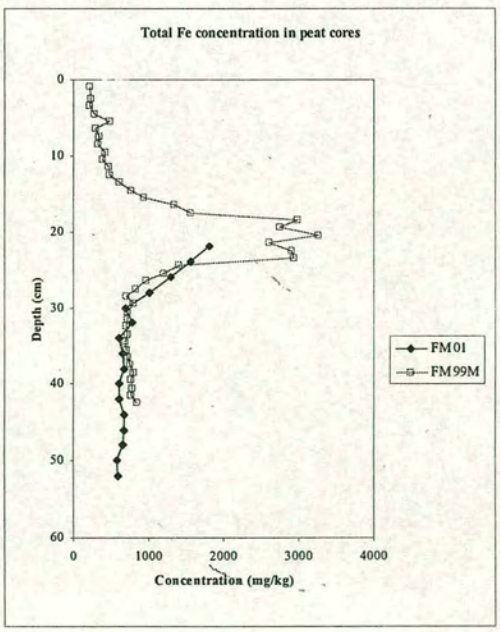


Figure 6.32 Depth profiles of Fe concentration in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

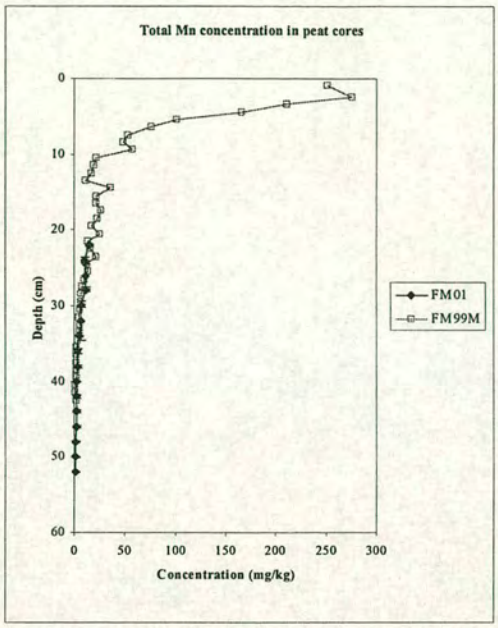


Figure 6.33 Depth profiles of Mn concentration in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

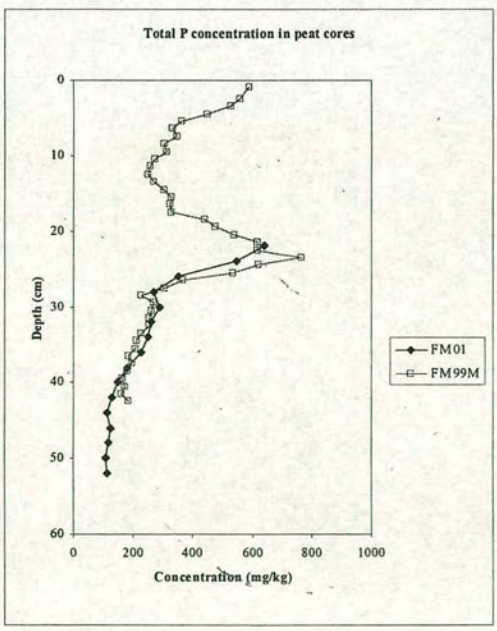


Figure 6.34 Depth profiles of P concentration in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

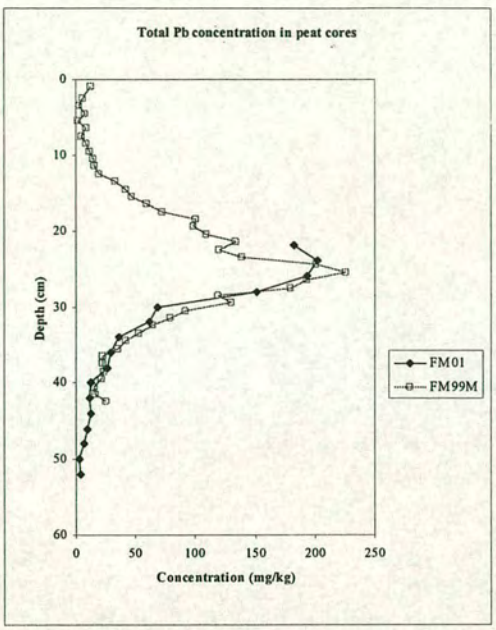


Figure 6.35 Depth profiles of Pb concentration in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

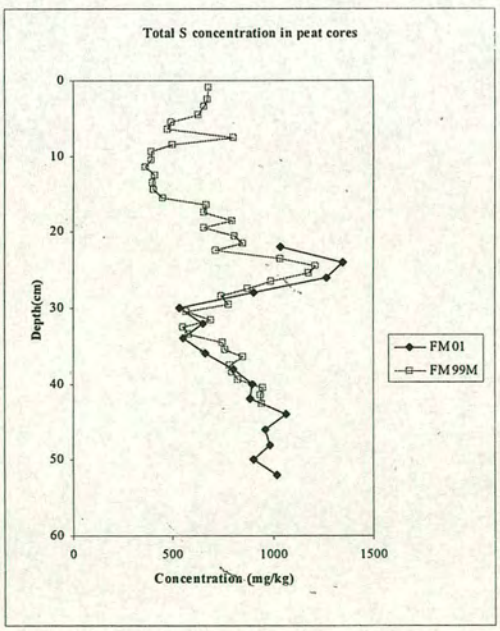


Figure 6.36 Depth profiles of S concentration in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

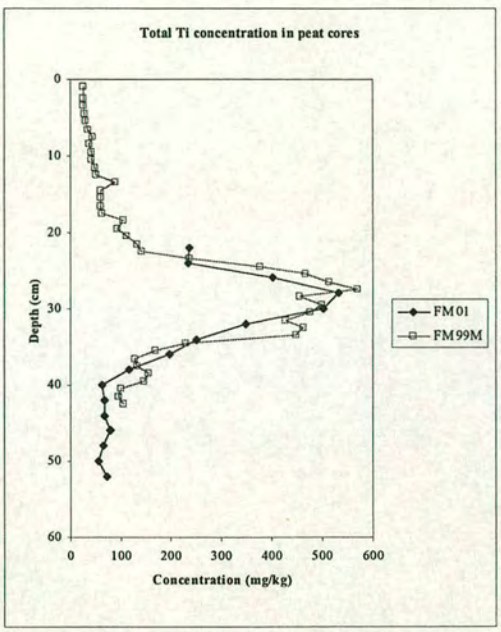


Figure 6.37 Depth profiles of Ti concentration in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

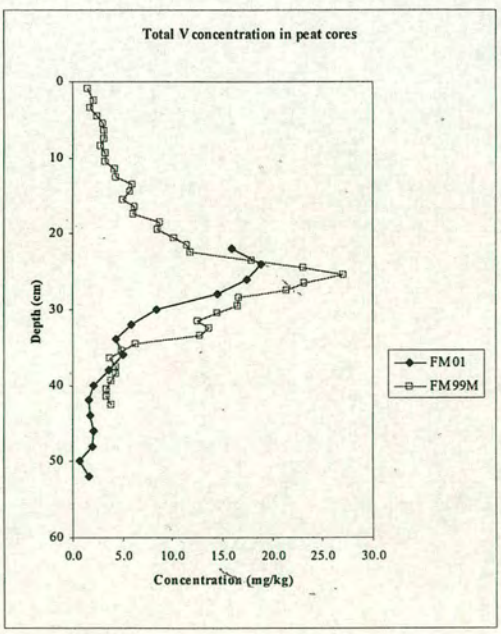


Figure 6.38 Depth profiles of V concentration in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

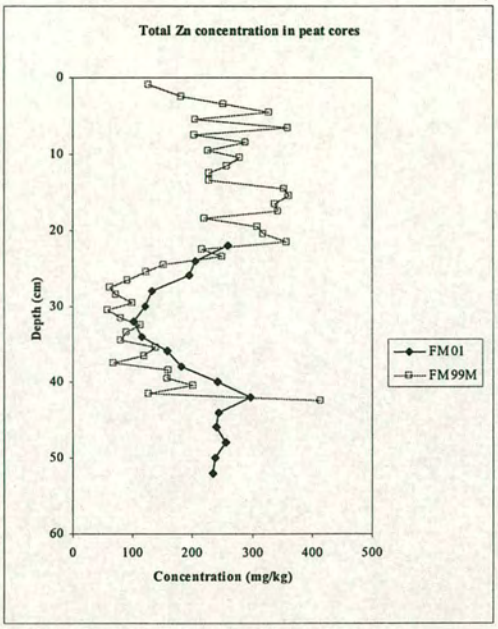


Figure 6.39 Depth profiles of Zn concentration in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

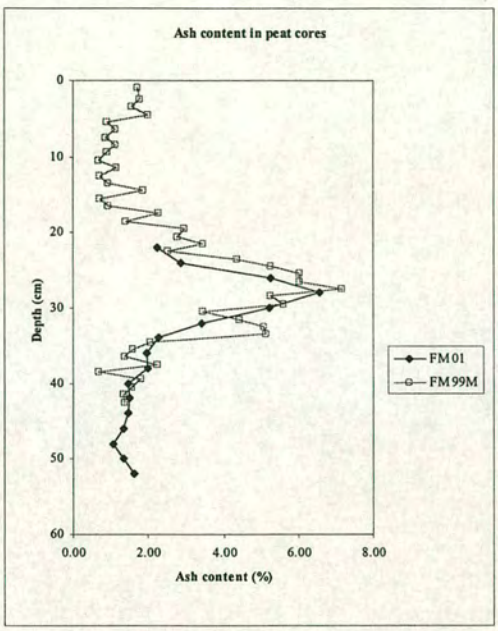


Figure 6.40 Depth profiles of ash content in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

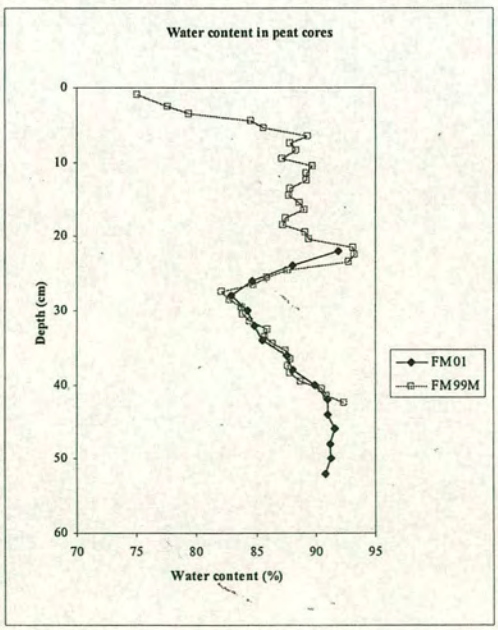


Figure 6.41 Depth profiles of water content in FM99M (0 – 43 cm) and in FM01 (0 – 32 cm), plotted with a 21 cm offset between the cores (i.e. FM01 0 – 32 cm becomes 21 – 53 cm).

In addition, when the inventories in g m^{-2} (calculated by summing sectional concentration x sectional weight ÷ cross sectional area of the core) are compared for the two cores, there is quite good agreement between them for 21 – 43 cm in the FM99M core and 0 – 22 cm in the FM01 core (Table 6.18). Again, this is good evidence for material (equivalent to 0 - 21 cm in the FM99M core) missing from the top of the FM01 core.

Table 6.18 Comparison of the inventories for selected elements in selected depth intervals of the FM99M and FM01 peat cores.

Element	FM99M 0-21 cm (g m^{-2})	FM99M 21-43 cm (g m^{-2})	FM99M 0-43 cm (g m^{-2})	FM01 0-22 cm (g m^{-2})	Inventory ratio FM99M (21-43 cm)/FM01 (0-22 cm)
Al	14.72	74.20	88.92	86.04	0.86
As	0.0166	0.0604	0.0770	0.0808	0.75
Cd	0.0110	0.0148	0.0258	0.0141	1.05
Cr	0.0222	0.1263	0.1485	0.1644	0.77
Cu	0.0756	0.1619	0.2375	0.2687	0.60
Fe	19.78	24.47	44.25	23.90	1.02
Mn	0.890	0.168	1.058	0.186	0.90
P	6.03	7.54	13.57	7.61	0.99
Pb	0.739	2.405	3.144	2.383	1.01
S	9.27	20.43	29.70	22.16	0.92
Ti	0.984	8.328	9.312	7.660	1.09
V	0.086	0.324	0.410	0.240	1.35
Zn	4.544	3.224	7.768	4.446	1.02

N.B. The mean ratio is 0.95 ± 0.19. These inventories have been derived from Table 3.11 and Table 6.5 – 6.13, correcting air-dried sectional weights using a moisture content of 9.9% (0 – 10 cm), 14.7% (10 – 21 cm) and 13.3% (21 – 43 cm) for FM99M and 12.2% (0 – 22 cm) for FM01.

In attempting to account for the absence of material from the top of FM01, there may be several contributory influences:

(i) it is known that vegetation (predominantly grass) was removed prior to collection of the FM01 core (Section 6.2),

(ii) there may have been differences in the surface of the bog (i.e. topography) at the sites chosen to collect the cores by the two different coring methods (monolith; Cuttle and Malcolm),

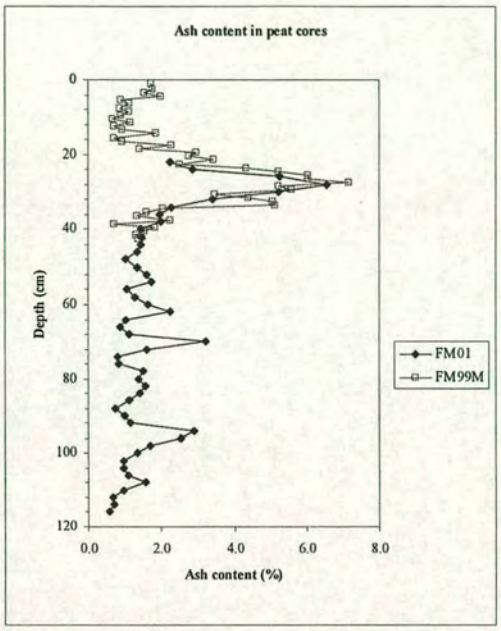
(iii) at the spots where the two corers were inserted, the surface vegetation itself may have been different,

(iv) the Cuttle and Malcolm corer tends to compress vegetation when pushed into the ground.

Furthermore, from other work on Flanders Moss peat bog, there is additional supporting evidence. In 1999, a Cuttle and Malcolm core, which had only a 2 cm plug of vegetation discarded after collection, was also low in ^{210}Pb inventory and derived flux (61 Bq $m^{-2}y^{-1}$) (Freeman, 2001). Another core, taken at the same time as the FM01 core and which had less vegetation (~ 7 cm) removed before collection, exhibited profiles closely matching those of the FM01 core, after allowing for an offset of ~ 4 cm. Finally, the data from another monolith core, collected in 1996, were in good agreement with the 1999 monolith (FM99M) core, after allowing for a 3 cm offset.

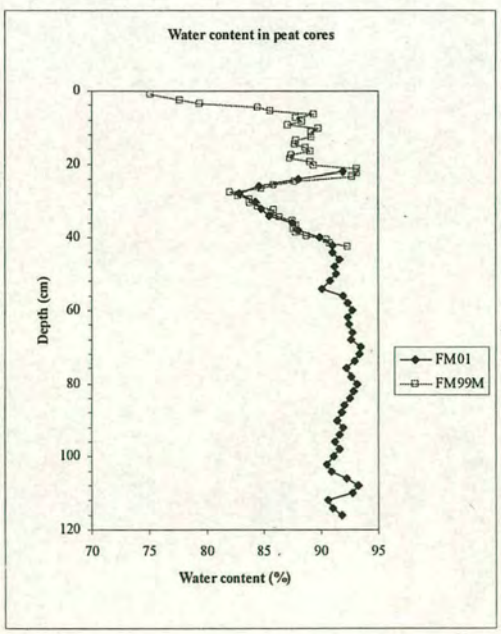
6.9.3 Interpretation of the Flanders Moss peat core profiles

Vertical depth profiles (ash content, water content, elemental concentrations, and $^{206}Pb/^{207}Pb$) for the entire length of the FM99M (0 – 43 cm) and FM01 (0 – 96 cm) cores are plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm) in Figs. 6.42 – 6.57.



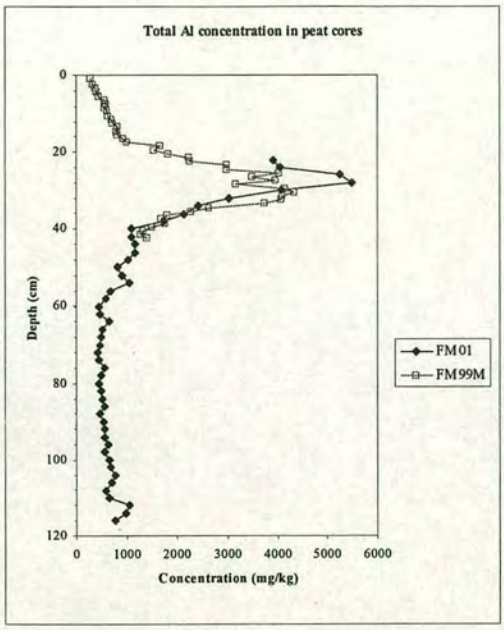
The ash content (Fig. 6.42) increases from values of ~ 0.5 % at depth (with noticeable peaks > 2 % at 94 cm, 70 cm, and 62 cm) to a pronounced peak between 25 and 34 cm, with a maximum of ~ 7 % at 27 – 28 cm. It then declines to values of ~ 0.5 % before increasing slightly to 1.7 % at the surface.

Figure 6.42 Depth profiles of ash content in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



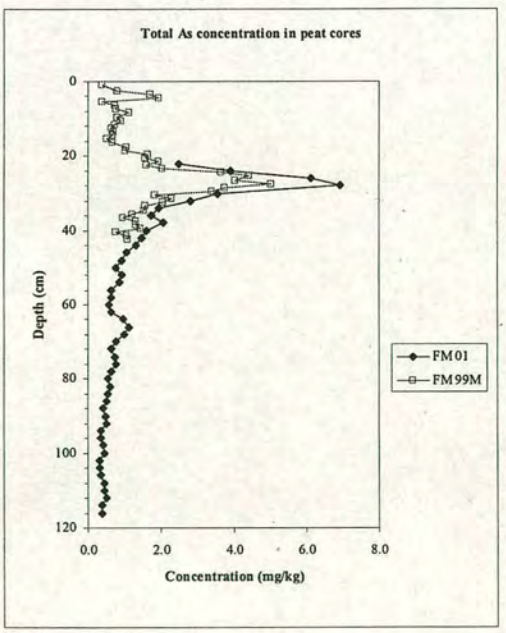
The water content (Fig. 6.43) is fairly constant at 90 – 94 % from depth to ~ 40 cm. There is then a decline to ~ 82 % at 27 – 28 cm, largely coincident with the marked increase in the ash content (Fig 6.42). The water content then peaks at 21 – 23 cm before declining slightly to a fairly constant value of ~ 88 % from 6 – 20 cm and then steeply to a minimum value of 75 % at the surface.

Figure 6.43 Depth profiles of water content in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



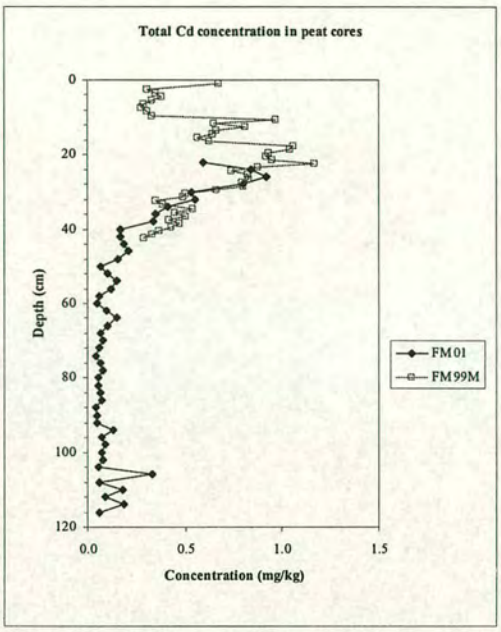
The Al concentration (Fig. 6.44) decreases from values of ~ 1000 mg/kg at 111 – 117 cm to 400 – 500 mg/kg at ~ 60 – 80 cm. There is then an increase to ~ 1100 mg/kg at ~ 40 cm followed by a rapid rise to a pronounced peak (18 – 40 cm) with a maximum of 4000 – 5500 mg/kg extending over several cm from 25 – 34 cm. Above 18 cm, the Al concentration then decreases slowly to ~ 300 mg/kg at the surface.

Figure 6.44 Depth profiles of Al concentration in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



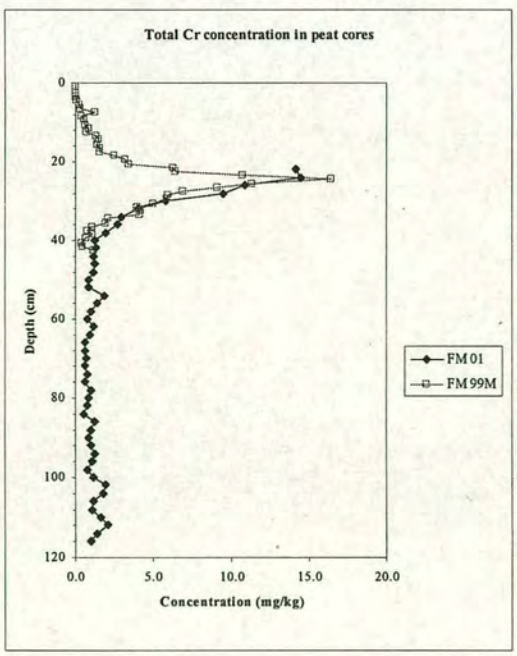
The As concentration (Fig 6.45) increases slowly from values of 0.3 – 0.5 mg/kg at depth (with a little peak ~ 1 mg/kg at 63 – 69 cm) to ~ 1 mg/kg at ~ 45 cm. There is then a steady rise to ~ 2 mg/kg at 33 – 39 cm, followed by a steep increase to a maximum of ~ 5 – 7 mg/kg at 25 – 29 cm. Thereafter, a steep decline to ~ 2 mg/kg by ~ 20 cm is followed by fairly constant values of ~ 0.5 mg/kg and a minor peak of ~ 2 mg/kg at ~ 3 – 5 cm, and then a declines to ~ 0.3 mg/kg at the surface.

Figure 6.45 Depth profiles of As concentration in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



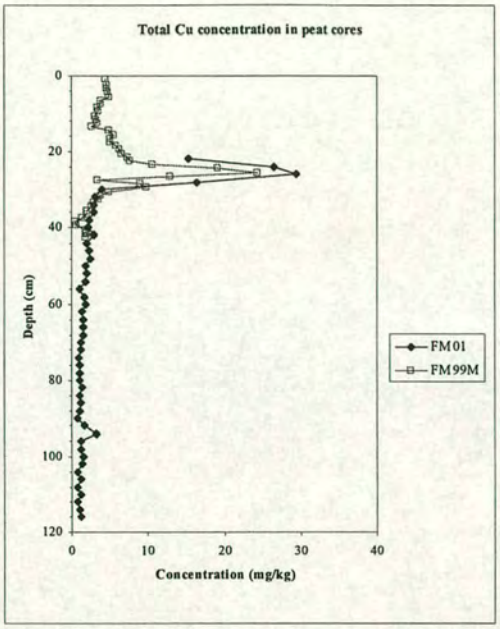
With the exception of a zone of irregular enhancement below 100 cm, Cd concentrations (Fig. 6.46) are generally < 0.1 mg/kg until ~ 65 cm. Thereafter, there is a slight increase to ~ 0.2 mg/kg by 40 cm, above where there is then a steady rise to ~ 1 mg/kg between 16 and 28 cm. Concentrations then fall a little irregularly to 0.6 mg/kg close to the surface.

Figure 6.46 Depth profiles of Cd concentration in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



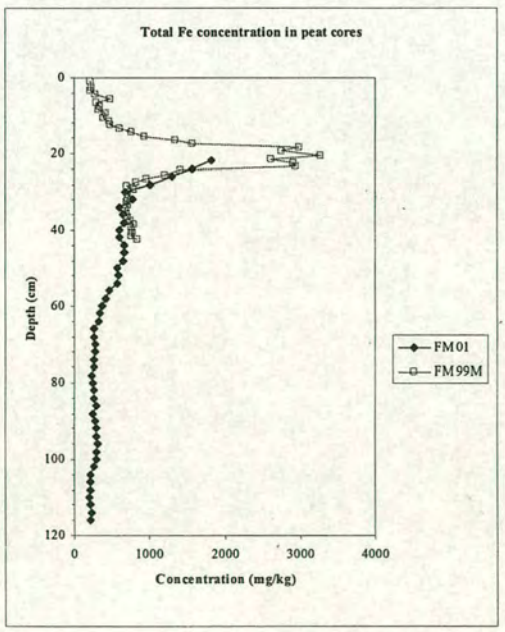
The Cr concentration (Fig. 6.47) decreases from values of ~ 1 – 2 mg/kg below 85 cm to values generally below or close to 1 mg/kg to ~ 40 cm. Thereafter, there is a steep increase to 14 – 16 mg/kg at 21 – 25 cm, followed by a steep decline to < 2 mg/kg at 17 – 18 cm and a steady decrease to < 0.5 mg/kg at surface.

Figure 6.47 Depth profiles of Cr concentration in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



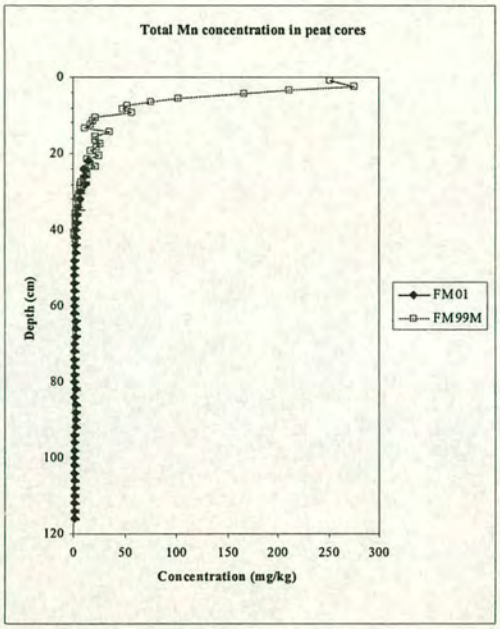
The Cu concentration (Fig. 6.48) is generally 1 – 2 mg/kg up to ~ 55 cm. Thereafter 2 – 4 mg/kg is maintained to ~ 30 cm, above which there is a steep increase to ~ 30 mg/kg at 25 – 27 cm. A rapid decline to ~ 7 mg/kg by ~ 22 cm is followed by a steady decrease to concentrations of 3 – 5 mg/kg in the top 10 cm.

Figure 6.48 Depth profiles of Cu concentration in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



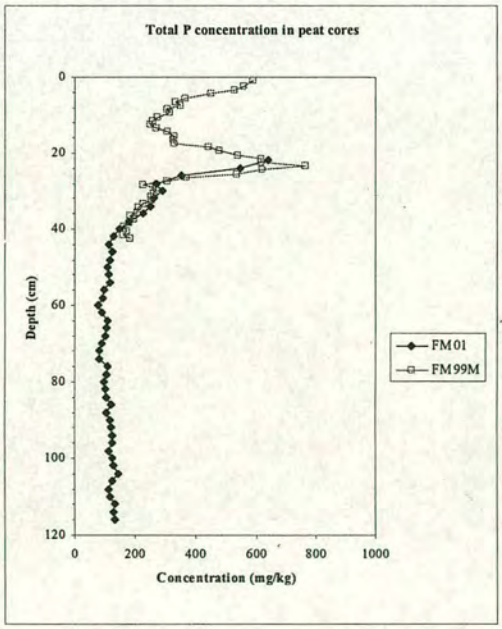
The Fe concentration (Fig. 6.49) is between 200 and 300 mg/kg up to ~ 65 cm. There is then a steady increase to ~ 700 mg/kg by ~ 30 cm, followed by a rapid rise to a pronounced peak of ~ 3000 mg/kg extending over 18 – 24 cm. A rapid decline to ~ 500 mg/kg by 13 cm is followed by a gentle decrease to concentrations slightly above 200 mg/kg at the surface.

Figure 6.49 Depth profiles of Fe concentration in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



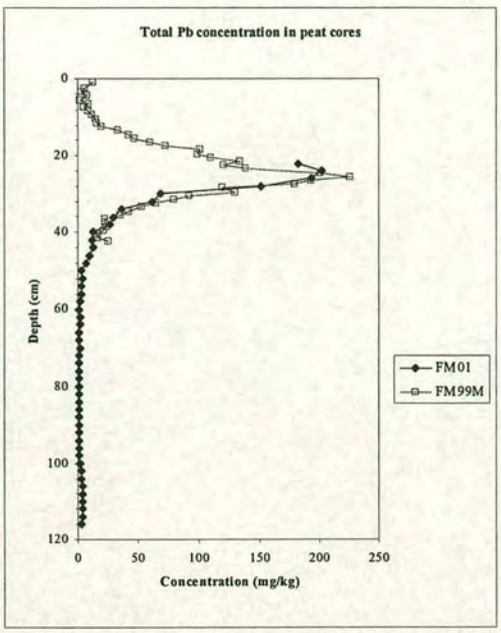
The Mn concentration (Fig. 6.50) generally lies from 1 – 3 mg/kg up to ~ 35 cm. Above this, there is then a steady rise to a small peak of ~ 35 mg/kg at 14 – 15 cm. A decline to 12 – 22 mg/kg over 10 – 14 cm is then followed by a steep increase to 250 – 275 mg/kg at the surface.

Figure 6.50 Depth profiles of Mn concentration in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



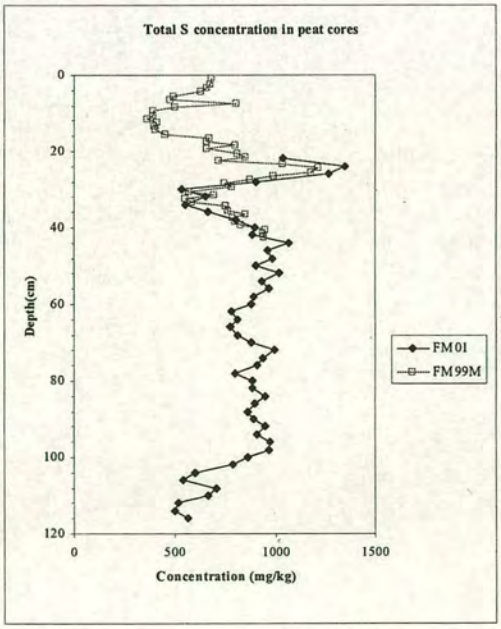
In general, the P concentration (Fig. 6.51) shows a slight decrease from ~ 130 mg/kg at depth to ~ 100 mg/kg at ~ 60 cm. Above this, there is a slight increase to ~130 mg/kg by ~ 40 cm, a steady increase to ~ 270 mg/kg by ~ 27 cm and a steep increase to a peak of 650 – 750 mg/kg at 23 – 24 cm. A steep decline to a minimum of 250 mg/kg at 12 – 13 cm is followed by a steady increase to about 600 mg/kg at the surface.

Figure 6.51 Depth profiles of P concentration in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



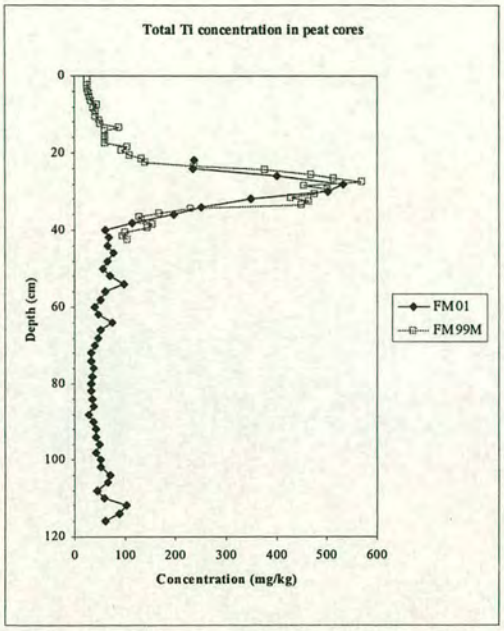
The Pb concentration (Fig. 6.52) is below 4 mg/kg up to 50 cm. Above this, a gradual increase to ~ 13 mg/kg by ~40 cm is followed by a steep increase to 200 – 225 mg/kg at ~ 25 cm. Thereafter, a steep decline to ~ 20 mg/kg at 12 – 13 cm is followed by a steady decrease to values generally < 10 mg/kg.

Figure 6.52 Depth profiles of Pb concentration in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



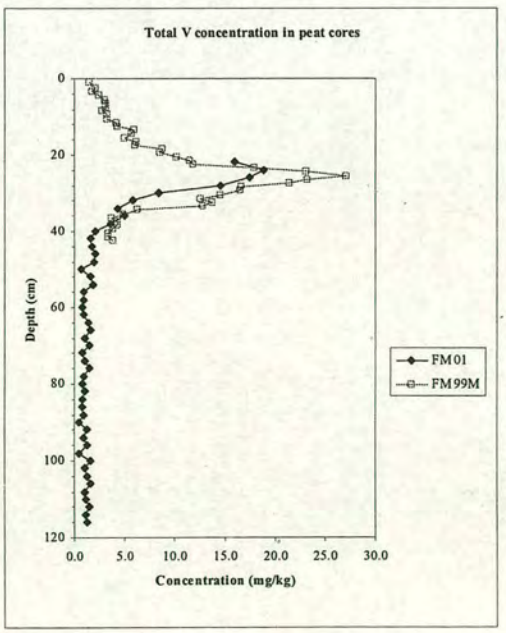
The S concentration (Fig. 6.53) increases from values of 500 – 700 mg/kg (103 – 117 cm) to 700 – 1000 mg/kg over the depth interval from 103 cm to 43 cm. There is then a steep decline to ~ 530 mg/kg at ~ 30 cm followed by a steep increase to a maximum of 1200 – 1350 mg/kg at 23 – 27 cm. A decrease to ~ 400 mg/kg (9 – 15 cm) is then followed by a slight increase towards the surface, punctuated by a peak of ~ 800 mg/kg at 8 cm.

Figure 6.53 Depth profiles of S concentration in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



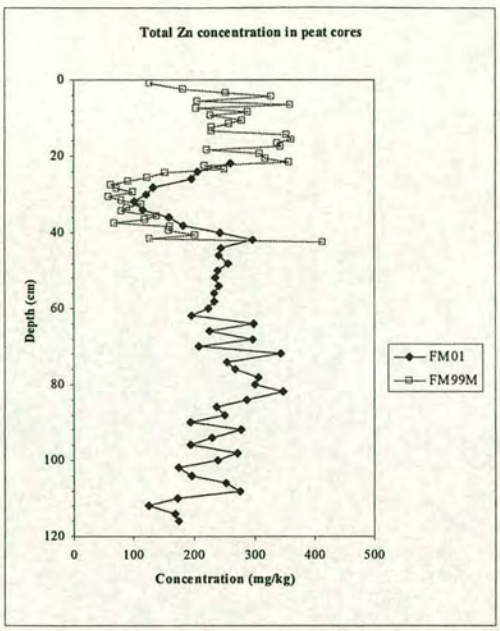
The Ti concentration (Fig. 6.54) falls from a peak of ~ 100 mg/kg (111 – 113 cm) to 30 – 40 mg/kg from 70 – 90 cm. Above this, there is an increase to ~ 70 mg/kg by 40 cm, followed by a steep increase to a peak of 450 – 570 mg/kg extending over 25 – 34 cm. A steep decline to ~ 60 mg/kg by ~ 18 cm is followed by a gentle decrease to 25 mg/kg at the surface.

Figure 6.54 Depth profiles of Ti concentration in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



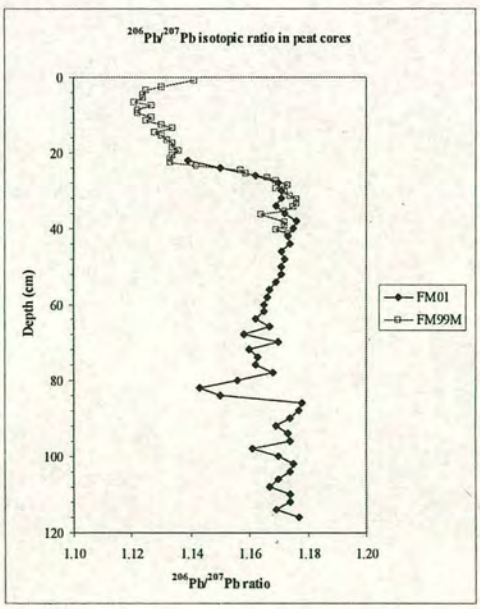
The V concentration (Fig. 6.55) is generally below 2 mg/kg up to ~ 40 cm, above which there is a steep increase to a peak of 19 – 27 mg/kg from 24 – 28 cm. A steep decline to 6 mg/kg by ~ 18 cm is followed by a gentle decrease to ~ 2 mg/kg at the surface.

Figure 6.55 Depth profiles of V concentration in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



The Zn concentration (Fig. 6.56) appears to increase somewhat erratically from ~ 125 mg/kg to 300 – 350 mg/kg by ~ 65 cm. Thereafter, a period of rather constant concentration of 200 – 300 mg/kg up to ~ 43 cm is followed by a sharp decline to values of 50 – 100 mg/kg from 26 to 35 cm. A steady increase to ~ 350 mg/kg by 21 – 22 cm is then followed by somewhat erratic concentrations in the range 200 – 350 mg/kg before a decline to ~ 125 mg/kg at the surface.

Figure 6.56 Depth profiles of Zn concentration in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).



The $^{206}Pb/^{207}Pb$ ratio (Fig. 6.57) is fairly constant at ~ 1.170 from depth to ~ 86 cm. There is a pronounced minimum of ~ 1.140 at ~ 83 cm. The $^{206}Pb/^{207}Pb$ ratio gradually increases from ~ 1.160 at ~ 76 cm to ~ 1.175 at ~ 28 cm. There is a steep decline to ~ 1.130 by ~ 20 cm followed by a gentler decline to ~ 1.121 at ~ 6 cm. There is a reversal of direction and increase to ~ 1.140 at the surface.

Figure 6.57 Depth profiles of $^{206}Pb/^{207}Pb$ ratio in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).

6.9.3.1 Upper region of Flanders Moss peat

That there are significant differences in the full depth profiles of the different elements is quite clear from Figs. 6.42 – 6.57. It is instructive, however, to first discuss the upper portion of the peat profile (i.e. 0 – 52 cm), i.e. the main zone of anthropogenic influence, in order to distinguish between different types of influence and the relative position of concentration peaks.

Fig. 6.58 (H_2O, Fe, S, P, Mn) exhibits features attributable to the influences of nutrient uptake and post-depositional remobilisation. In the upper few cm of vegetation, where water content decreases noticeably, nutrient elements Mn and P are enriched and subject to recycling in the growing vegetation. This influence is perhaps slightly evident also for S, but is not really apparent for Fe. In contrast, Fe is highly enriched from 18 – 24 cm, noticeably in a zone of especially high water content, taken here to represent the position of the water table (note that the decline in water content below 24 cm is attributable to the increasing ash content in the core, as mentioned in Section 6.9.3 and discussed further below). It is postulated here that the Fe peak, which is clearly distinct from the peaks exhibited by heavy metal contaminants such as Pb and major/minor elements such as Al and Ti (see Figs. 6.59 and 6.60), results from post-depositional remobilisation of Fe under reducing conditions, followed by upwards diffusion, reoxidation and precipitation under more oxidising conditions at the level of the water table. The position of the Fe peak, spread over several cm, reflects the fluctuating height of the water table. Thus, although the Fe may have been introduced into the peat bog by atmospheric deposition, a temporal record of this input is not retained in the bog because of these post-depositional diagenetic effects. From the shape of the profiles also, it is just possible that P exhibits a similar diagenetic feature at 23 – 27 cm, i.e. appearing at the lower end of the Fe peak. It is known from work on lake sediments that the anionic phosphate can be released from association with Fe oxyhydroxides under reducing conditions and then diffuses upwards in similar fashion to dissolved Fe before becoming readsorbed when the latter oxidises and precipitates.

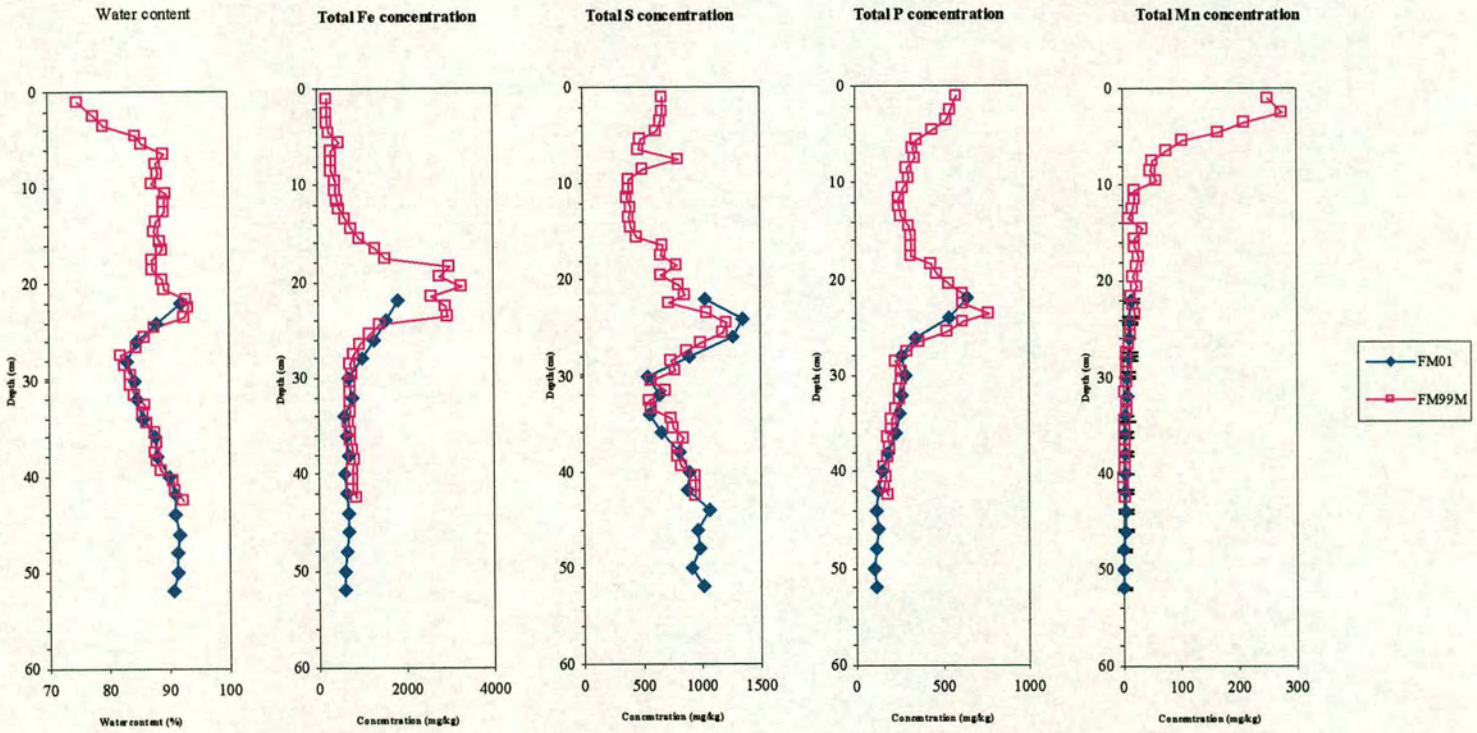


Figure 6.58 Vertical profiles of water content, Fe, S, P, and Mn in the upper region of Flanders Moss peat cores.

Certain elements (e.g. Cr, Cu, Pb, V), traditionally viewed as heavy metal contaminants associated with significant anthropogenic releases to the atmosphere from industry, energy generation and transport sources, all exhibit a marked concentration peak, some 5 cm below that of Fe, with maximum concentrations at a depth of 24 - 26 cm (Fig. 6.59), corresponding to the 1950s according to the corrected ^{210}Pb dating for the 2001 core (Table 6.17). It is noticeable that S also exhibits a concentration peak at this depth. There is thus strong evidence here, which will later be discussed in greater detail for Pb, of retention of a historical record of atmospheric deposition of heavy metal contaminants emanating from anthropogenic sources.

Another group with similar profiles is that of ash, Al, Ti and As (Fig. 6.60). The broad zone of enhancement extends from ~ 23 - 35 cm for ash, Al and Ti, and from ~ 24 - 30 cm for As. The concentration maxima appear at 27 - 28 cm (i.e. ca. 1940 according to Table 6.17), clearly below the maxima in the heavy metal concentrations (Fig. 6.59). Traditionally, the increase in ash content in the upper regions of peat is considered to arise from anthropogenic activities, including agricultural and other land uses as well as industry. Indeed, some workers use the Al and Ti concentrations as an indication of the extent of the contribution of soil dust associated with the former, e.g. in the clearing of land for agriculture and human settlement. The use and validity of this approach will be considered later.

The final group (H_2O, Cd, Zn, S) reveals some similarities (Fig. 6.61). The Cd and Zn profiles are fairly similar over the top 20 cm but thereafter the Cd profile is much closer to those of the heavy metal contaminants in Fig. 6.59, and indeed exhibits a peak at the same depth, along with the S maximum. While the Cd concentration then tails off with depth, both the Zn and S display similar-shaped profiles below 30 cm, a rapid decrease to a minimum at 32 cm, then increasing to a constant value by ~ 44 cm. It is suggested here that the profiles of the heavy metal contaminant Zn (and possibly Cd) introduced by atmospheric deposition do not reflect the historical input to the same extent as those of Cr, Cu, Pb and V in Fig 6.59. Indeed, the Zn (which may also be a micronutrient element) appears to be mobile (see also the lower region of the core, where elevated concentrations

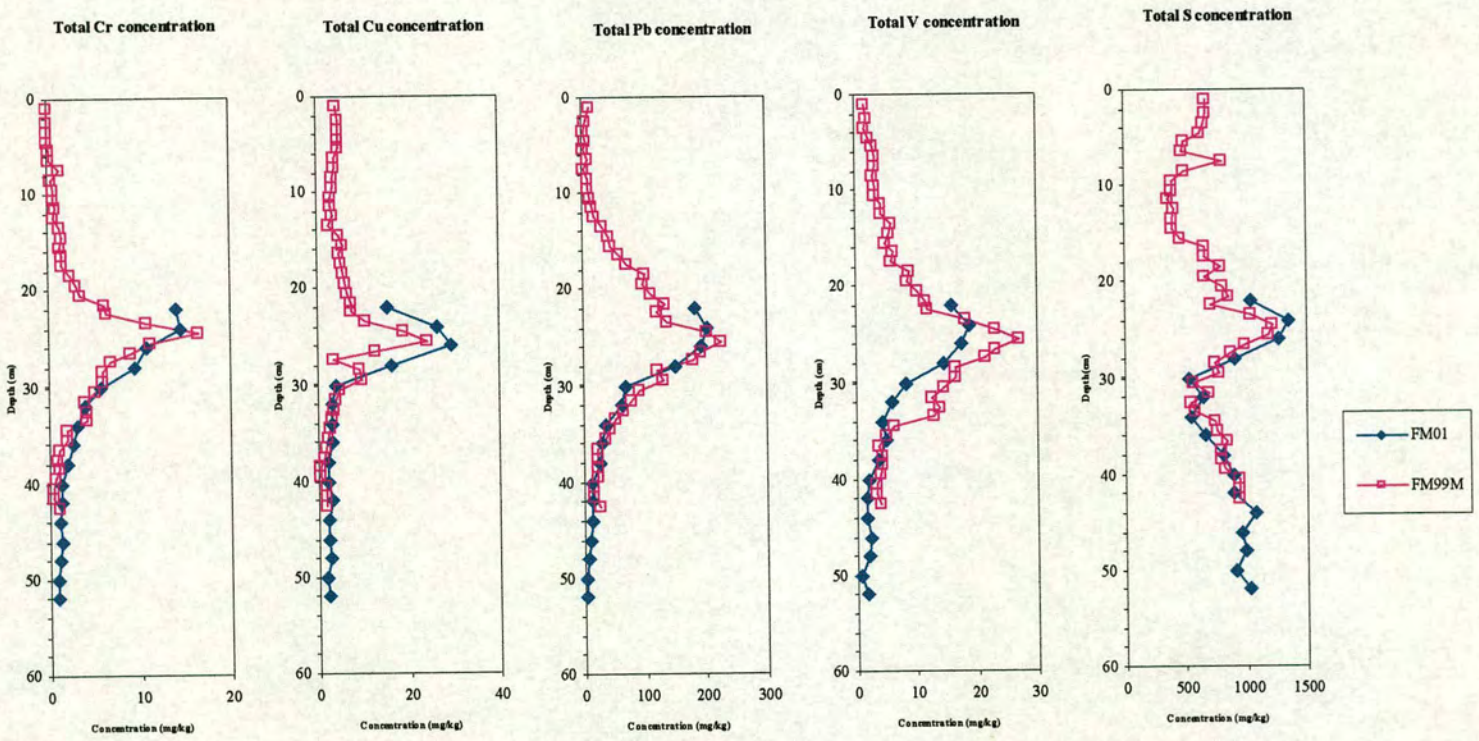


Figure 6.59 Vertical profiles of Cr, Cu, Pb, V, and S in the upper region of Flanders Moss peat cores.

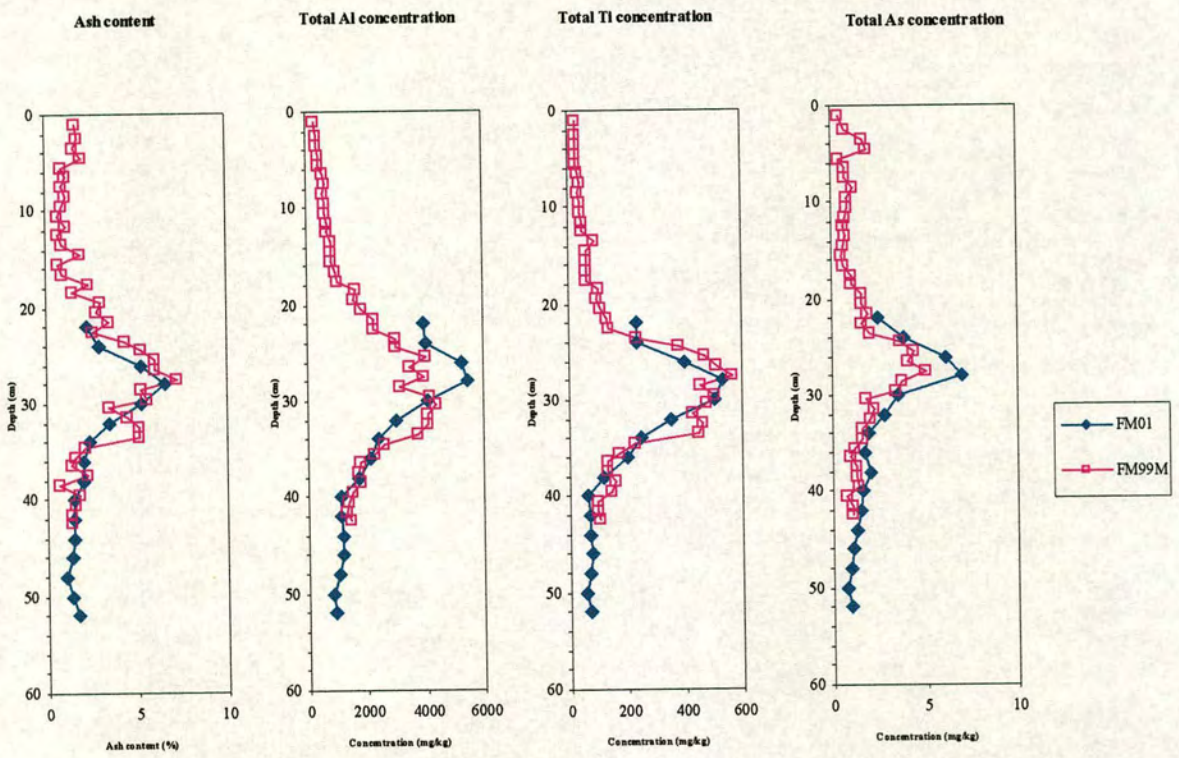


Figure 6.60 Vertical profiles of ash content, Al, Ti, and As in the upper region of Flanders Moss peat cores.

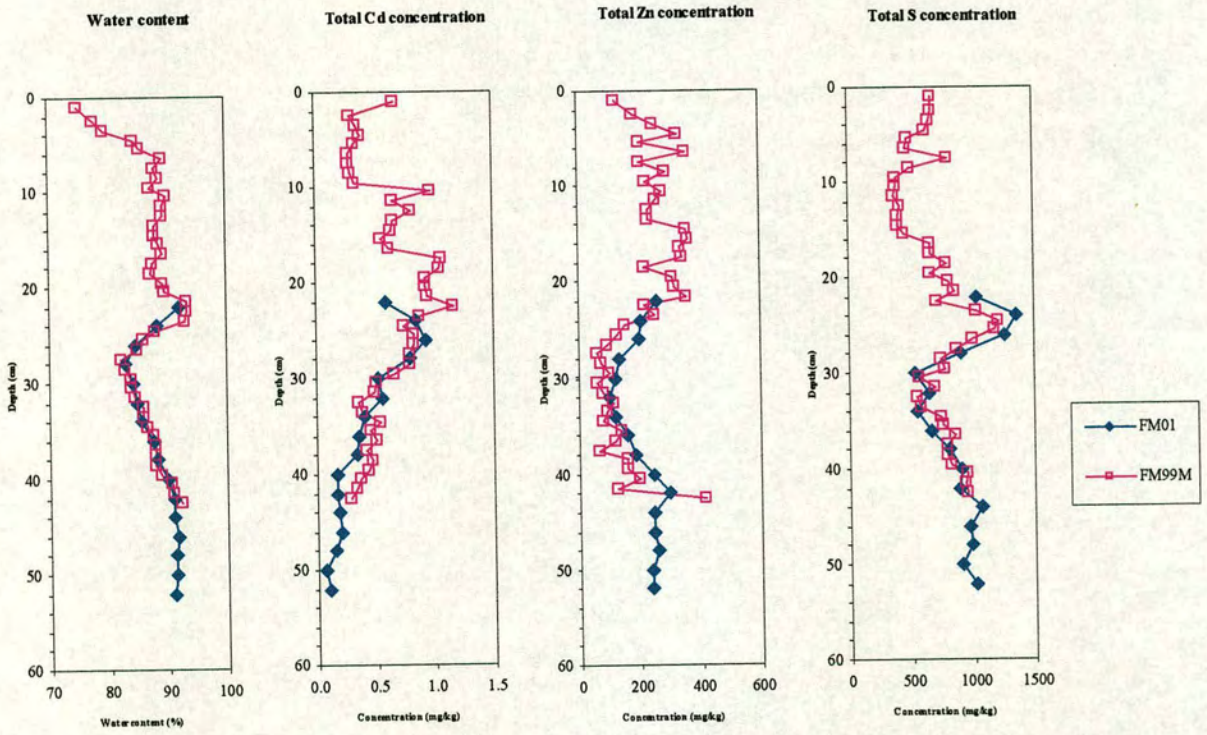


Figure 6.61 Vertical profiles of water content, Cd, Zn, and S in the upper region of Flanders Moss peat cores.

are found). Its apparent relationship with S in the reducing zones could reflect formation of Zn sulphides at depth. The general similarity between the shapes of the profiles for the water content, Zn and S from ~ 27 - 40 cm could also reflect a lower degree of association with the heavy metal contaminant peak than exhibited by Cd and the other heavy metals (Fig.6.59).

6.9.3.2 Lower region of Flanders Moss peat

For those elements for which sectional mean concentrations below 50 cm are sufficiently high and RSDs are sufficiently low, comparative profiles have been plotted in Fig. 6.62 (Ash, Al, Ti, Pb, As and Cd) and Fig. 6.63 (H_2O, Fe, Mn, P, S, Zn).

Somewhat surprisingly and in contrast to the upper region, the variations in the ash content, with peaks at 62, 70 and 94 cm, do not appear to be reflected in the Al and Ti profiles (Fig. 6.62). The shapes of both the Al and Ti profiles, however, are very similar to that of Pb and, to a lesser extent, of Cd, with peaks at 54 and 64 cm. The profile for As is similar to those of Al, Ti, Pb and Cd from 50 to ~ 75 cm but thereafter declines fairly steadily to constant values from ~ 95 cm to the bottom. This is in marked contrast to those for Al, Ti, Pb and, to a lesser extent, Cd, which exhibit a significant increase in concentration below ~ 100 cm and a discernible peak at 112 cm.

The profiles for Fe, S and Zn decrease, while that of P increases, slowly towards the bottom (Fig. 6.62). Mn, which is present in only trace amounts, not exceeding 3 mg/kg, exhibits small peaks at ~ 65 cm and ~ 90 cm. The former is close to that for Al, Ti, Pb and Cd. Otherwise, however, the profiles for the elements in Fig. 6.63 do not really resemble those of the elements in Fig. 6.62.

The mean concentration data for each of the above elements are summarised for four different depth zones (57 - 71 cm, 71 - 93 cm. 93 - 101 cm and 101 - 117 cm), largely chosen on the basis of observed variations in Pb concentration, in Table 6.19.

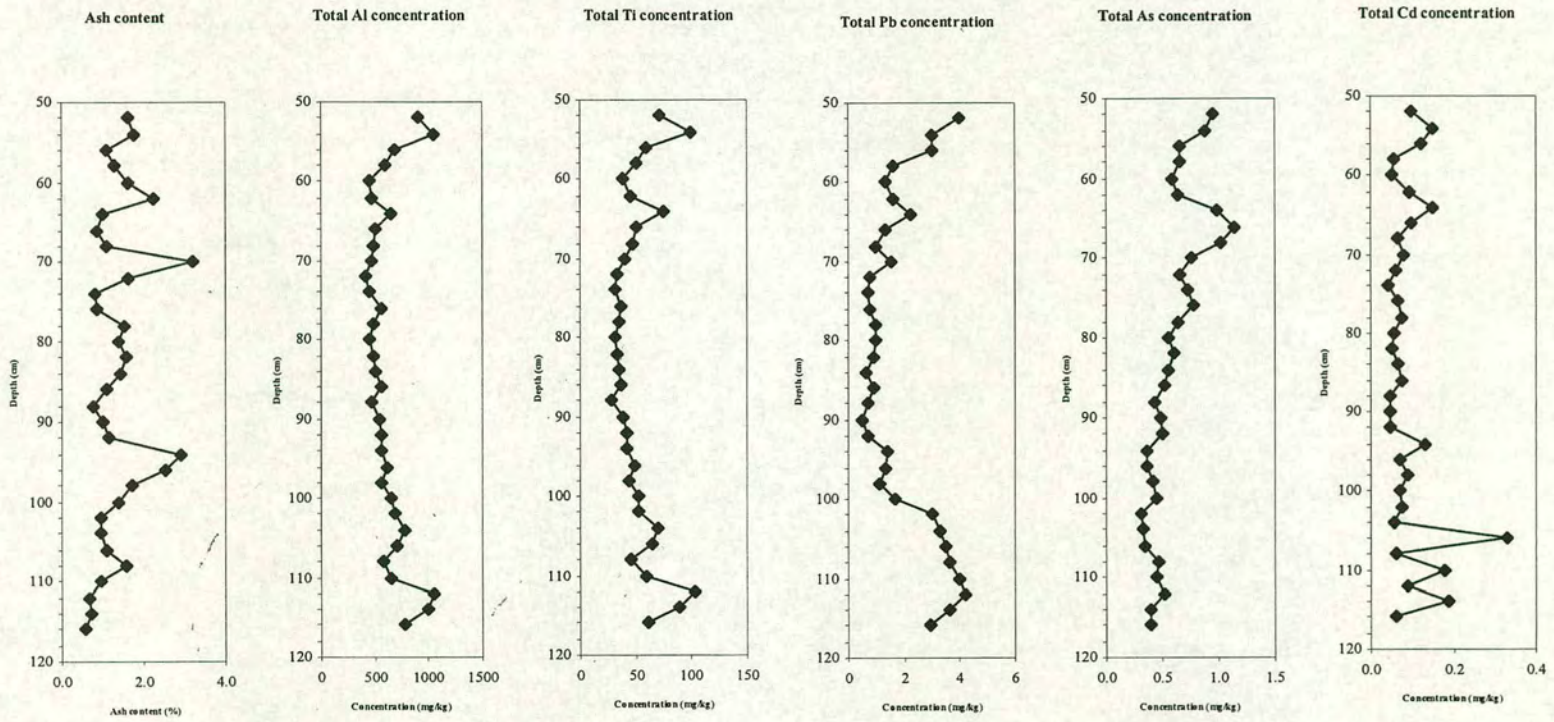


Figure 6.62 Vertical profiles of ash, Al, Ti, Pb, As, and Cd in the lower region of the Flanders Moss peat core collected in 2001.

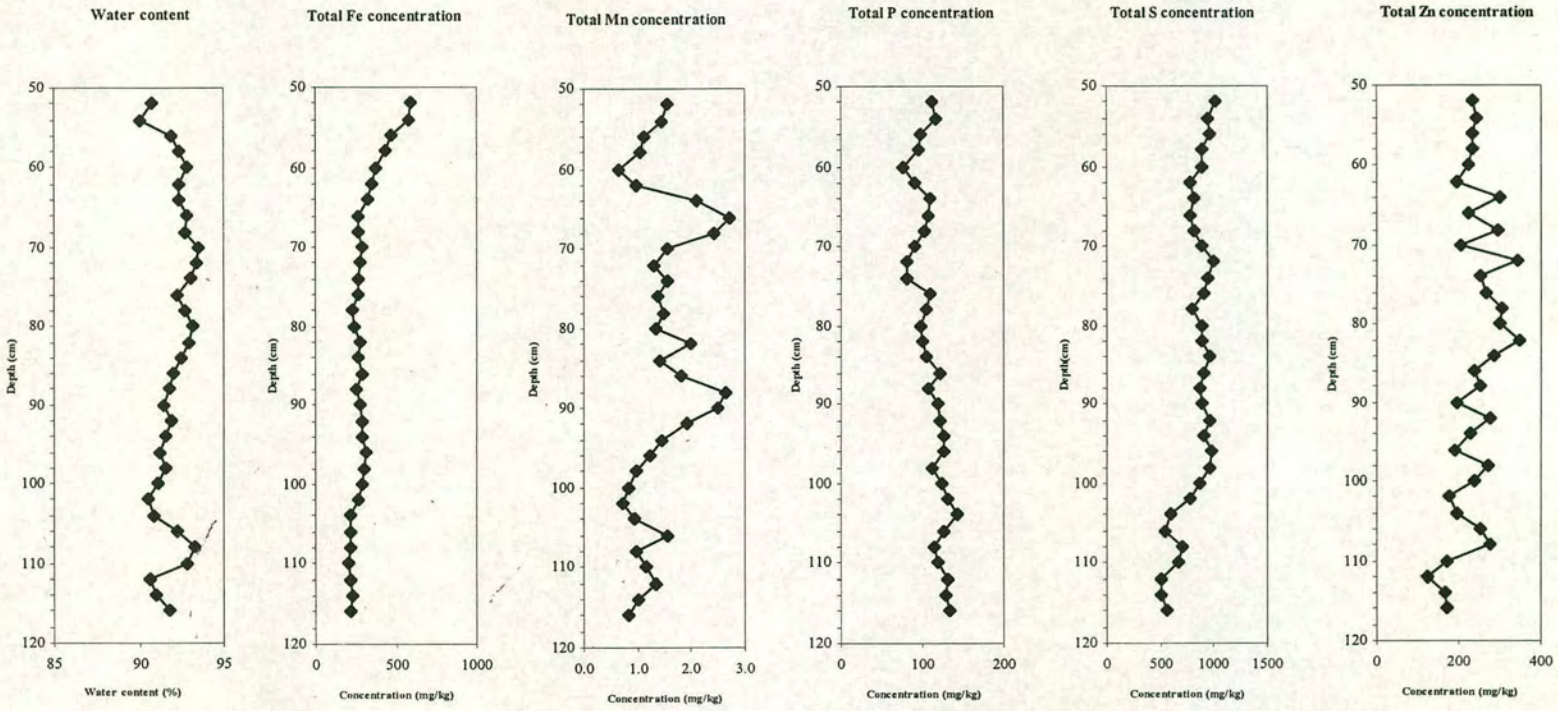


Figure 6.63 Vertical profiles of water content, Fe, Mn, P, S, and Zn in the lower region of the Flanders Moss peat core collected in 2001.

Table 6.19 Summary of elemental concentration data and element/Ti and element/Al ratios for different depth zones of the lower region of Flanders Moss peat.

Depth	57-71 cm	71-93 cm	93-101 cm	101-117 cm
Ti (mg/kg)	49.7 ± 11.7 ----------	34.5 ± 3.9 **41.5 ± 10.1**	46.3 ± 5.1 ----------	67.9 ± 19.1
Al (mg/kg)	517 ± 75 ----------	500 ± 50 **523 ± 67**	597 ± 46 ----------	777 ± 165
Ti/Al	0.097 ± 0.011 ----------	0.069 ± 0.005 **0.081 ± 0.013**	0.077 ± 0.003 ----------	0.087 ± 0.008 ----------
Pb (mg/kg)	1.50 ± 0.37 ----------	0.78 ± 0.16 **1.11 ± 0.43**	1.38 ± 0.25 ----------	3.51 ± 0.45
Pb/Ti	0.030 ± 0.006 ----------	0.023 ± 0.005 **0.027 ± 0.006**	0.030 ± 0.004 ----------	0.055 ± 0.014
Pb/Al	0.0029 ± 0.0005 ----------	0.0016 ± 0.0004 **0.0021 ± 0.0007**	0.0023 ± 0.0003 ----------	0.0047 ± 0.0010
As (mg/kg)	0.82 ± 0.22	0.59 ± 0.11	0.40 ± 0.05	0.40 ± 0.07
As/Ti	0.017 ± 0.004	0.017 ± 0.003	0.009 ± 0.001	0.006 ± 0.002
As/Al	0.0016 ± 0.0004	0.0011 ± 0.0002	0.0007 ± 0.0001	0.0005 ± 0.0001
Cd (mg/kg)	0.085 ± 0.034 ----------	0.058 ± 0.012 **0.073 ± 0.027**	0.091 ± 0.029 ----------	0.131 ± 0.097
Cd/Ti	0.0017 ± 0.0004 ----------	0.0017 ± 0.0004 **0.0018 ± 0.0008**	0.0020 ± 0.0009 ----------	0.0020 ± 0.0015 ----------
Cd/Al	0.00016 ± 0.00005 ----------	0.00012 ± 0.00002 **0.00015 ± 0.00008**	0.00016 ± 0.00006 ----------	0.00017 ± 0.00014 ----------
Fe (mg/kg)	329 ± 59 ----------	268 ± 18 **293 ± 44**	297 ± 9 ----------	224 ± 16
Fe/Ti	6.87 ± 1.80 ----------	7.82 ± 0.73 **7.27 ± 1.26**	6.48 ± 0.70 ----------	3.51 ± 0.98
Fe/Al	0.64 ± 0.12 ----------	0.54 ± 0.05 **0.57 ± 0.09**	0.50 ± 0.04 ----------	0.30 ± 0.06
Mn (mgkg)	1.64 ± 0.78	1.75 ± 0.46	1.13 ± 0.30	1.06 ± 0.26
Mn/Ti	0.033 ± 0.015	0.051 ± 0.016	0.025 ± 0.009	0.016 ± 0.005
Mn/Al	0.0032 ± 0.0015	0.0035 ± 0.0009	0.0019 ± 0.0006	0.0014 ± 0.0004
P (mg/kg)	96 ± 11	104 ± 14	122 ± 6	128± 9
P/Ti	1.97 ± 0.26	3.03 ± 0.36	2.66 ± 0.28	2.00 ± 0.45
P/Al	0.187 ± 0.020 ----------	0.208 ± 0.014 **0.193 ± 0.025**	0.205 ± 0.015 ----------	0.170 ± 0.027 ----------
S (mg/kg)	830 ± 50 ----------	906 ± 53 **885 ± 64**	926 ± 54 ----------	608 ± 126
S/Ti	17.4 ± 4.0	26.5 ± 3.0	20.2 ± 2.7	9.8 ± 3.9
S/Al	1.63 ± 0.24 ----------	1.83 ± 0.24 **1.72 ± 0.25**	1.56 ± 0.17 ----------	0.83 ± 0.27
Zn (mg/kg)	239 ± 42 ----------	278 ± 46 **258 ± 46**	233 ± 33 ----------	192 ± 49
Zn/Ti	4.92 ± 0.84	8.18 ± 1.72	5.11 ± 1.05	3.13 ± 1.46
Zn/Al	0.465 ± 0.070	0.566 ± 0.132	0.393 ± 0.072	0.264 ± 0.109

Key features of the mean concentration data are as follows:

- Ti is enhanced in the 101 - 117 zone (67.9 ± 19.1 mg/kg) compared with 57 - 101 cm (41.5 ± 10.1 mg/kg)
- Al is enhanced in the 101 - 117 zone (777 ± 165 mg/kg) compared with 57 - 101 cm (523 ± 67 mg/kg)
- Pb is enhanced in the 101 - 117 zone (3.51 ± 0.45 mg/kg) compared with 57 - 101 cm (1.11 ± 0.43 mg/kg)
- Cd is possibly enhanced in the 101 - 117 zone (0.131 ± 0.097 mg/kg) compared with 57 - 101 cm (0.073 ± 0.027 mg/kg)
- As, Fe, Mn, S and Zn are generally lower in the 101 - 117 cm zone than in the preceding zones; P is slightly higher.

Also included in Table 6.19 are calculated mean element/Ti and element/Al ratios for the different zones. The ratios for individual sections are also plotted for the entire lower depth region in Figs. 6.64 and 6.65.

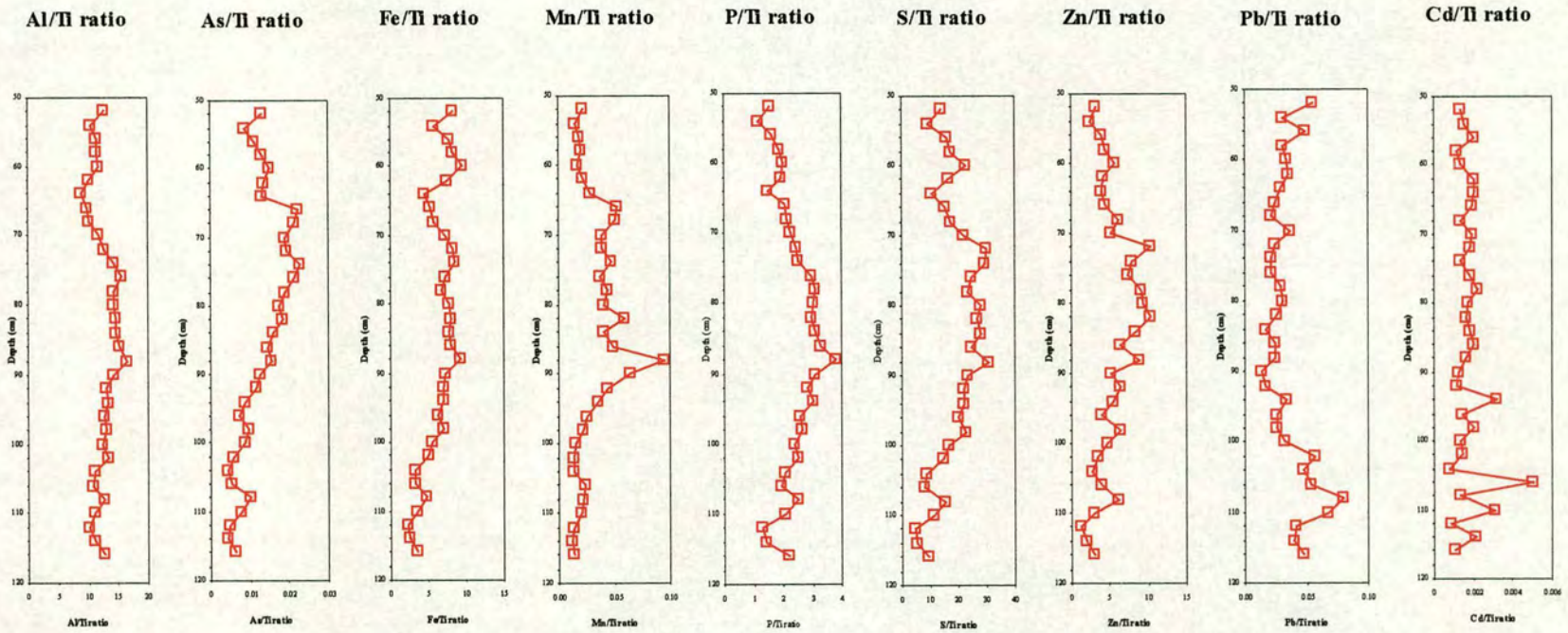


Figure 6.64 Vertical profiles of Al/Ti, As/Ti, Fe/Ti, Mn/Ti, P/Ti, S/Ti, Zn/Ti, Pb/Ti, and Cd/Ti ratios in the lower region of the Flanders Moss peat core collected in 2001.

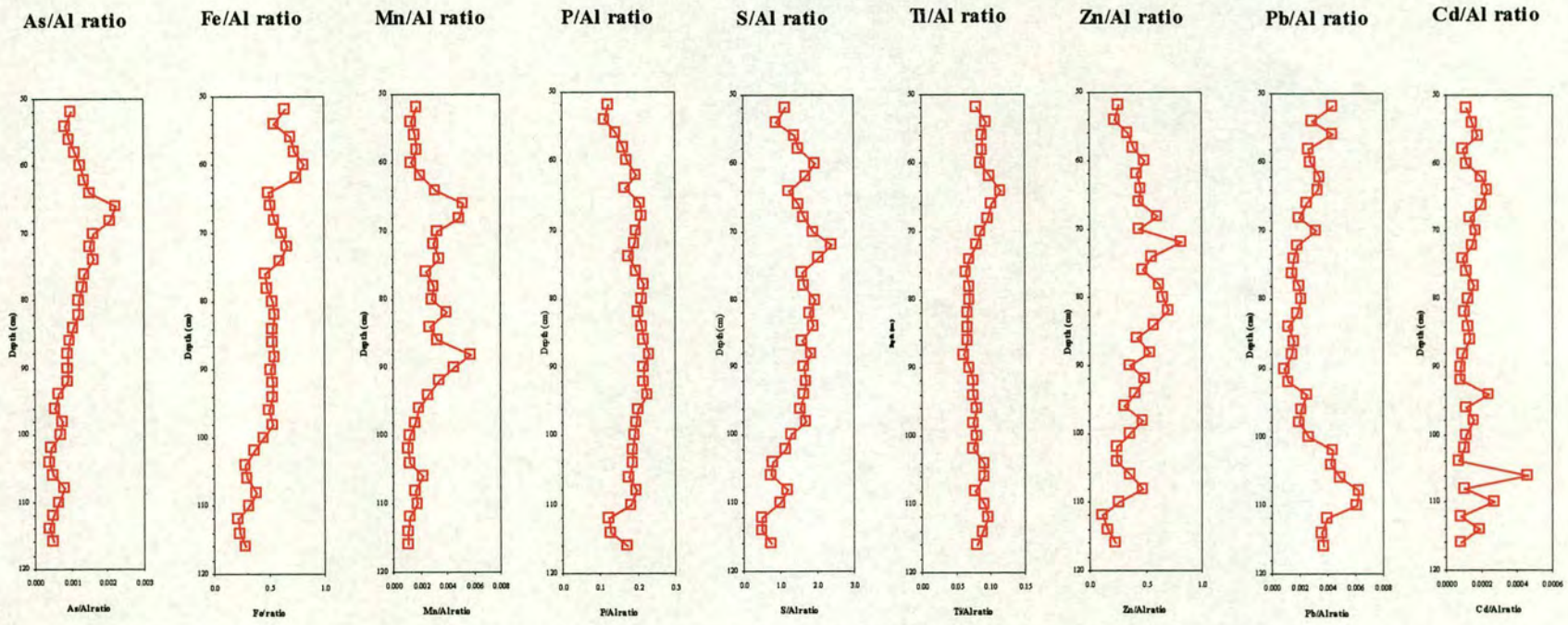


Figure 6.65 Vertical profiles of As/Al, Fe/Al, Mn/Al, P/Al, S/Al, Ti/Al, Zn/Al, Pb/Al, and Cd/Al ratios in the lower region of the Flanders Moss peat core collected in 2001.

Key features of the mean ratio data and ratio profiles are as follows:

- apparent enhancements in mean element/Ti ratios (Fig. 6.64) for As, Fe, Mn, S and Zn in the 57 - 101 cm region, but especially for the 71 - 93 cm zone, are largely attributable to (i) a small decrease in the mean Ti concentration for the 71-93 cm zone and (ii) both a decrease in mean element concentration and a significant increase in mean Ti concentration for the 101 - 117 cm zone.
- there are similar enhancements for element/Al ratios (Fig. 6.65) for As, Fe, Mn, S and Zn in the 57 - 101 cm region, but those of the 71 - 93 cm zone do not stand out so much from those of the 57 - 71 cm and 93 - 101 cm zones as the mean Al concentration for the 71 - 93 cm zone does not exhibit the decrease seen in the mean Ti concentration for that zone (Table 6.19). Hence the apparent slight increase for Al/Ti in the middle of the lower region (Fig. 6.64). This corresponds to a mean Ti/Al ratio of 0.069 ± 0.005 for the 71 - 93 cm zone, but, overall, the mean Ti/Al ratio for the entire 57 - 117 cm region is fairly constant at 0.081 ± 0.013.
- the mean Pb/Ti ratio for the 101 - 117 cm zone is 0.055 ± 0.014, compared with 0.027 ± 0.006 for the 57 - 101 cm zone (any variation between the mean ratios for the 57 - 71 cm, 71 - 93 cm and 93 - 101 cm zones being largely insignificant). Similarly, the mean Pb/Al ratio for the 101 - 117 cm zone is 0.0047 ± 0.0010, compared with 0.0021 ± 0.0007 for the 57 - 101 cm zone. These ratios, along with the increase in the mean Pb concentration for the 101 - 117 cm zone will be discussed (along with corresponding $^{206}Pb/^{207}Pb$ data) in more detail in Sections 6.9.4 and 6.9.5.
- the mean Cd/Ti and mean Cd/Al ratios do not vary across the different zones.

The next Section will focus upon variations in the concentrations of selected elements Al, Ti, Pb and As and the corresponding Ti/Al, Pb/Ti, Pb/Al, As/Ti and As/Al ratios for the complete depth profile from 0 - 117 cm (i.e. 0 - 43 cm for FM99M and 21 - 117 cm for FM01).

6.9.4 Intercomparison of Al, Ti, Pb and As in the Flanders Moss peat profile

The Al concentration, Ti concentration and Ti/Al ratio are plotted for 0 - 117 cm (i.e. 0 - 43 cm from FM99M and 21 - 117 cm from FM01) in Fig. 6.66. The broad zone of elevated Al and Ti concentrations is from 18 - 40 cm, with the highest concentrations (3,500 - 5,000 mg/kg and 450 - 550 mg/kg, respectively) in the 25 - 34 cm region. Traditionally, the presence of these elements has been associated with inputs of dust (e.g. from soil) to the peat bog surface. The presence of highly elevated concentrations of Al and Ti (coincident with an elevated ash peak), such as those observed here, are commonly thought to result from inputs of soil dust associated with greatly increased anthropogenic activity. Some workers use Al or Ti (or other 'conservative' elements) to normalise the concentrations of other elements and then to derive 'enrichment factors' via a comparison of measured element/Al or element/Ti ratios with values for the Earth's crust. The Ti/Al ratio for the Earth's continental crust is 0.050, resulting from average concentrations of 4,010 and 79,600 mg/kg, respectively (Wedepohl, 1995). This ratio is similar to that observed for the lower region of the Flanders Moss peat (Table 6.19, Fig. 6.65).

There are, however, two principal zones of enhancement of the Ti/Al ratio, namely (i) from 24 - 34 cm (mean Ti/Al = 0.125 ± 0.015) in the FM99M core and from 25 - 35 cm (i.e. 4 - 14 cm) (mean Ti/Al = 0.103 ± 0.018) in the FM01 core and (ii) from 51 - 73 cm (i.e. 30 - 52 cm) (mean Ti/Al = 0.093 ± 0.011) in the FM01 core. While zone (i) is associated with greatly enhanced concentrations, zone (ii) is clearly not (Table 6.19). If, on the basis of the mean Ti/Al ratio of 0.081 ± 0.013 calculated for 57 - 117 cm, the Ti concentrations are predicted from the measured Al concentrations, a region of "excess" Ti is obtained from 24 - 35 cm (on the basis of the FM99M core) and from 27 - 37 cm (on the basis of the FM01 core, with a 21 cm offset) (Fig. 6.67). If a mean Ti/Al ratio of 0.069 ± 0.005 (i.e. corresponding to the region of minimum Ti concentration in the profile, 71 - 93 cm) is used, the region of "excess" Ti is slightly larger, at 23 - 36 cm (from FM99M) and 25 - 37 cm (from FM01). The maximum "excess" Ti concentration is at 27 - 28 cm (FM99M) and 29 - 31 cm (FM01) (Fig. 6.68).

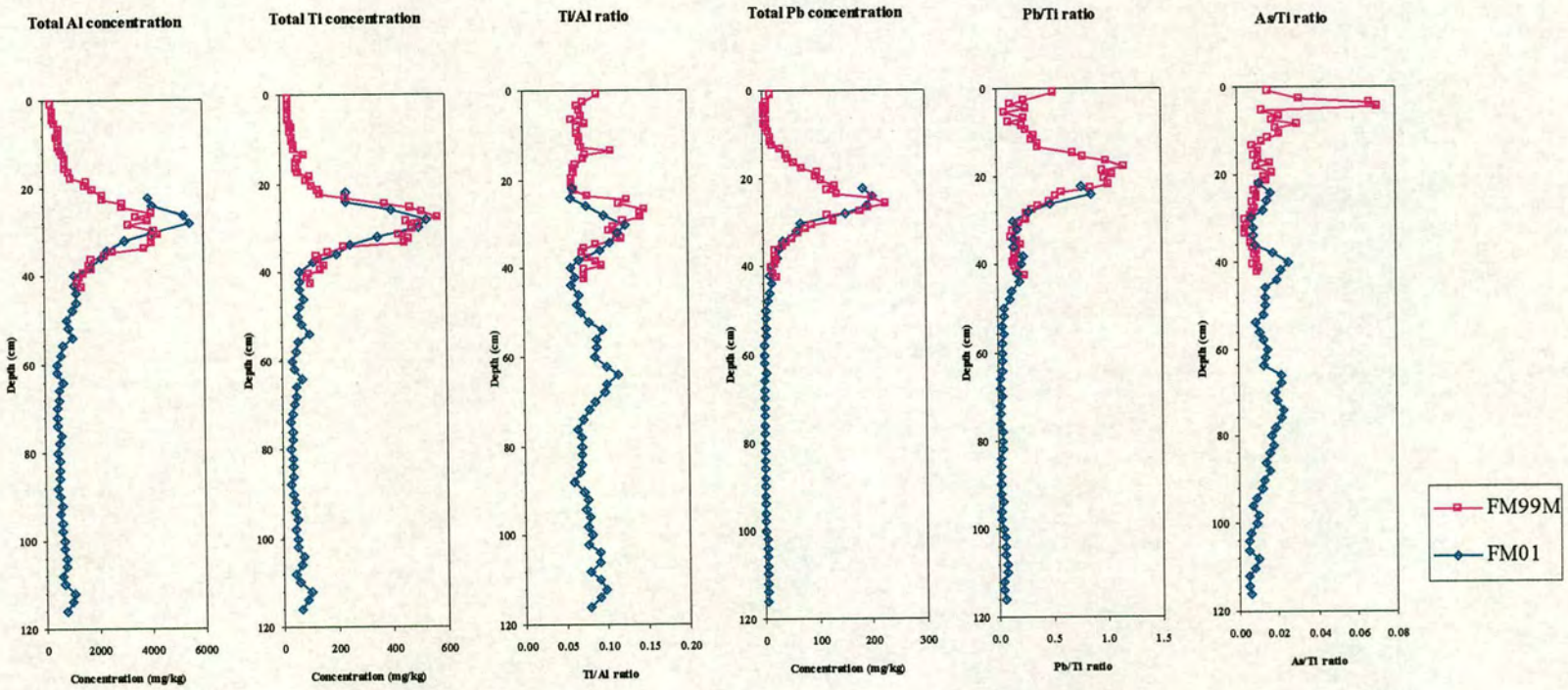


Figure 6.66 Vertical profiles of Al, Ti, and Pb concentration, Ti/Al, Pb/Ti, and As/Ti ratios in FM99M (0 – 43 cm) and FM01 (0 – 96 cm) plotted with a 21 cm offset between the cores (i.e. FM01 0 – 96 cm becomes 21 – 117 cm).

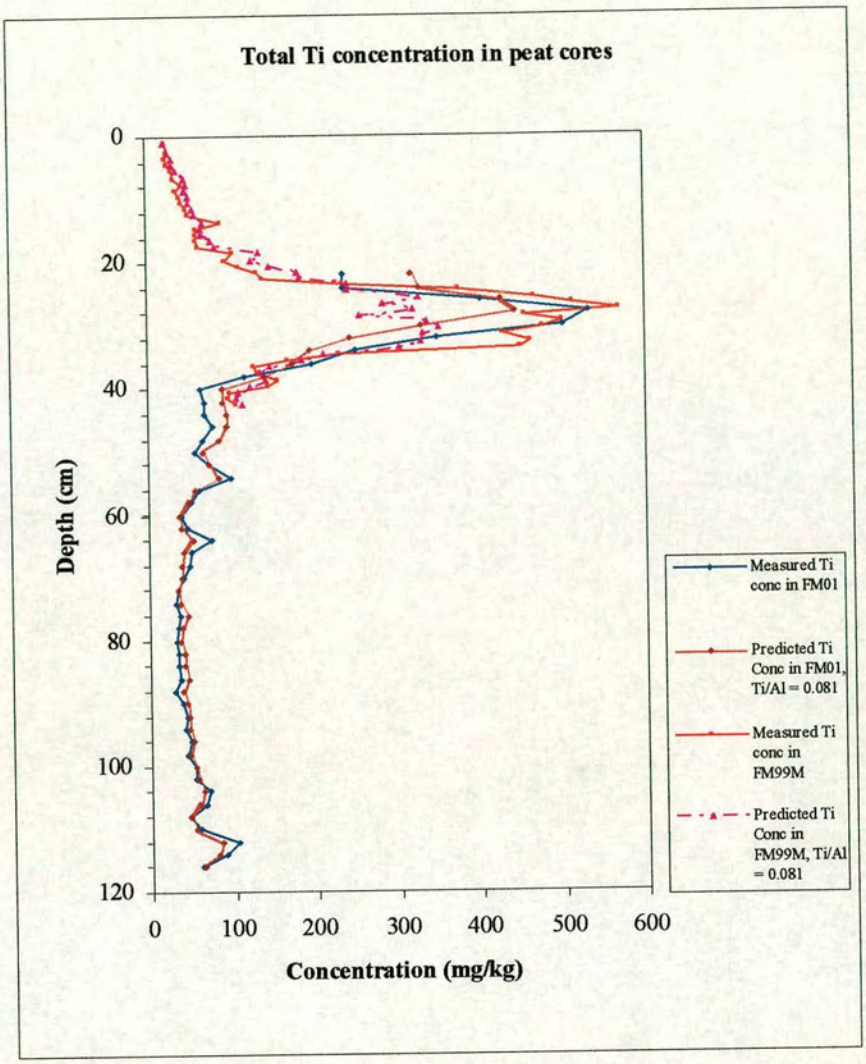


Figure 6.67 A comparison of measured and predicted Ti concentrations (based on a mean Ti/Al ratio of 0.081 for 57 - 117 cm and measured Al concentrations).

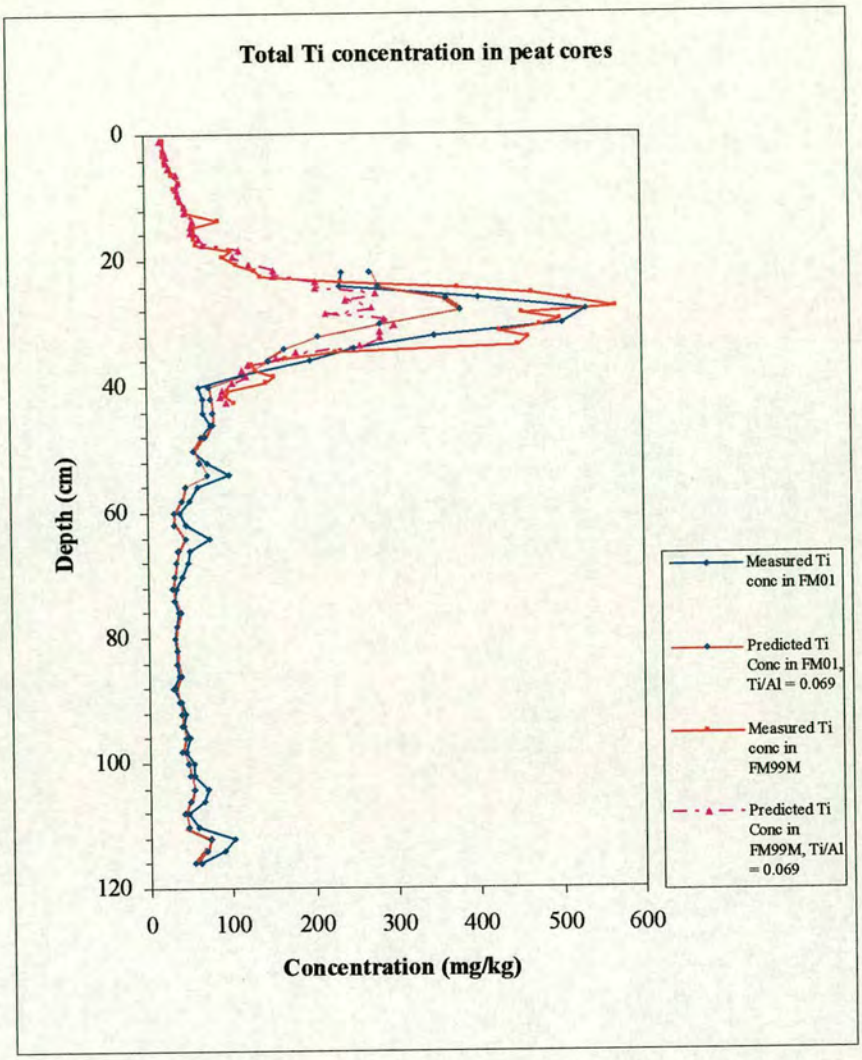


Figure 6.68 A comparison of measured and predicted Ti concentrations (based on a mean Ti/Al ratio of 0.069 for 71 - 93 cm and measured Al concentrations).

It is interesting to note that the maximum Pb concentrations, however, are at 25 - 26 cm (FM99M) and 23 - 25 cm (FM01) (Fig. 6.59), but the maximum As concentrations are lower in the core, at 27 - 28 cm (FM99M) and 27 - 29 cm (FM01) (Fig. 6.60), and therefore closer to the maximum "excess" Ti concentrations. There is therefore a suggestion here that Ti has been enriched relative to Al in this region of the profile and, in view of the associated elevated maximum concentrations of As, that coal burning may have made a contribution to both Ti and As, especially from 23 - 30 cm. It may be that processes involved in the release of Ti and Al from coal, or subsequently in the

atmosphere, have contributed to the alteration of the Ti/Al ratio. What is clear, however, is that the As concentration peak (FM99M, 27 - 28 cm; FM01, 27 - 29 cm) occurs below the Pb concentration peak (FM99M, 25 - 26 cm; FM01, 23 - 25 cm) and that the latter occurs below the Pb/Ti maximum (mean 1.033 ± 0.070) from 16 - 22 cm (Fig. 6.66). This maximum Pb/Ti ratio is almost 40 times that of the mean value for 57 - 101 cm and, indeed, 280 times that of the average Pb/Ti ratio of the Earth's crust. The relative positioning of the Pb/Ti and Pb peaks will be considered in more detail in terms of the historical record of Pb deposition in Section 6.9.5.

At the bottom of the peat profile (101 - 117 cm), the increase in the Pb/Ti ratio to 0.055 ± 0.014 from the overlying value of 0.027 ± 0.006, along with an increase in the Pb concentration to 3.51 ± 0.45 mg/kg from 1.11 ± 0.43 mg/kg, is indicative of Pb input from a source other than soil dust, perhaps Pb mining and smelting. This, too, will be considered further in Section 6.9.5, but it is worth noting that arsenic on this occasion shows an increase in neither concentration nor As/Ti ratio; indeed, the latter decreases (Table 6.19).

6.9.5 Historical record of Pb deposition in Flanders Moss peat

The Pb concentration profile shown in Fig. 6.66 is overwhelmingly influenced in the upper region (i.e. to at least 57 cm) by contributions from anthropogenic Pb sources (e.g. car-exhaust emissions, fossil fuel combustion, smelting etc). Below that even the low concentrations (<3 mg/kg; mean 1.1 ± 0.43 mg/kg) recorded from 57 - 101 cm may well have been influenced by anthropogenic Pb, as the Pb/Ti ratio of 0.027 ± 0.006 is an order of magnitude greater than the crustal Pb/Ti ratio of 0.0037 (i.e. 14.8/4,010). From 101 - 117 cm, the elevated Pb concentrations (2.9 - 4.2 mg/kg; mean 3.51 ± 0.45 mg/kg) and the elevated Pb/Ti ratio of 0.055 ± 0.014 are indicative of anthropogenic influence. Unfortunately, the ~ 1 m depth of the profile renders it impossible to determine the Pb concentration and Pb/Ti ratio prior to that suggested mining/smelting episode. On the basis of the crustal and mean 57 - 101 cm Pb/Ti ratios, however, it is possible, on the assumption that all variations in Ti are attributable to variations in soil dust input (i.e. ignoring any possible fossil fuel contributions to Ti), to calculate a range of predicted

values for the soil-dust-related Pb concentration for each Flanders Moss peat section. For the maximum Pb concentrations of 226 mg/kg at 25 - 26 cm (FM99M) and of 202 mg/kg at 23 - 25 cm (FM01, i.e. originally 2 - 4 cm), this amounts to no more than 1.7 - 12.6 mg/kg and 0.9 - 6.3 mg/kg, respectively. For the maximum Ti concentrations of 569 mg/kg at 27 - 28 cm (FM99M) and of 532 mg/kg at 27 - 29 cm (FM01, i.e. originally 6 - 8 cm), this amounts to a calculated contribution to the Pb concentration of no more than 2.1 - 15.4 mg/kg and 2.0 - 14.4 mg/kg for measured Pb concentrations of 180 mg/kg and 151 mg/kg, respectively. This approach to the use of conservative element (e.g. Ti) data, i.e. the calculation of a soil-dust contribution (whether the result of anthropogenic or natural influences) to the concentration of Pb in each peat section is here considered more acceptable than that of the presentation of the depth profiles of Pb in the form of calculated enrichment factors (i.e. quotients).

6.9.5.1 The industrial and post-industrial periods

There is a plot of Ti concentration, total Pb concentration, Pb/Ti ratio, $^{206}Pb/^{207}Pb$ and As concentration versus depth (0 - 117 cm) in Flanders Moss peat in Fig. 6.69. It is instructive first to consider these entities, however, for that portion of the Flanders Moss peat profile subjected to the strongest anthropogenic influence and for which "corrected" ^{210}Pb dates are available, i.e. 21-35 cm, corresponding to the 100 years from 1876 to 1976 (Table 6.17). The dates have been appended to the $^{206}Pb/^{207}Pb$ values (corresponding to the mid-points of 2-cm sections) for the FM01 core that was ^{210}Pb-dated. The plot in Fig. 6.70 is actually from 15 - 40 cm to enable trends just above and below the dated zone to be apparent.

From 40 to 35 cm (corresponding to the 19th and possibly pre-19th century):

- the Ti concentration, which is elevated above the mean, 41.5 ± 10.1 mg/kg, for 57 - 101 cm, increases from ~ 100 to ~ 200 mg/kg
- the Pb concentration, which is elevated above the mean, 1.11 ± 0.43 mg/kg, for 57 - 101 cm, increases from ~ 15 to ~ 40 mg/kg
- the Pb/Ti ratio, which is elevated above the mean, 0.027 ± 0.006, for 57 - 101 cm, stays fairly constant at ~ 0.15 - 0.20

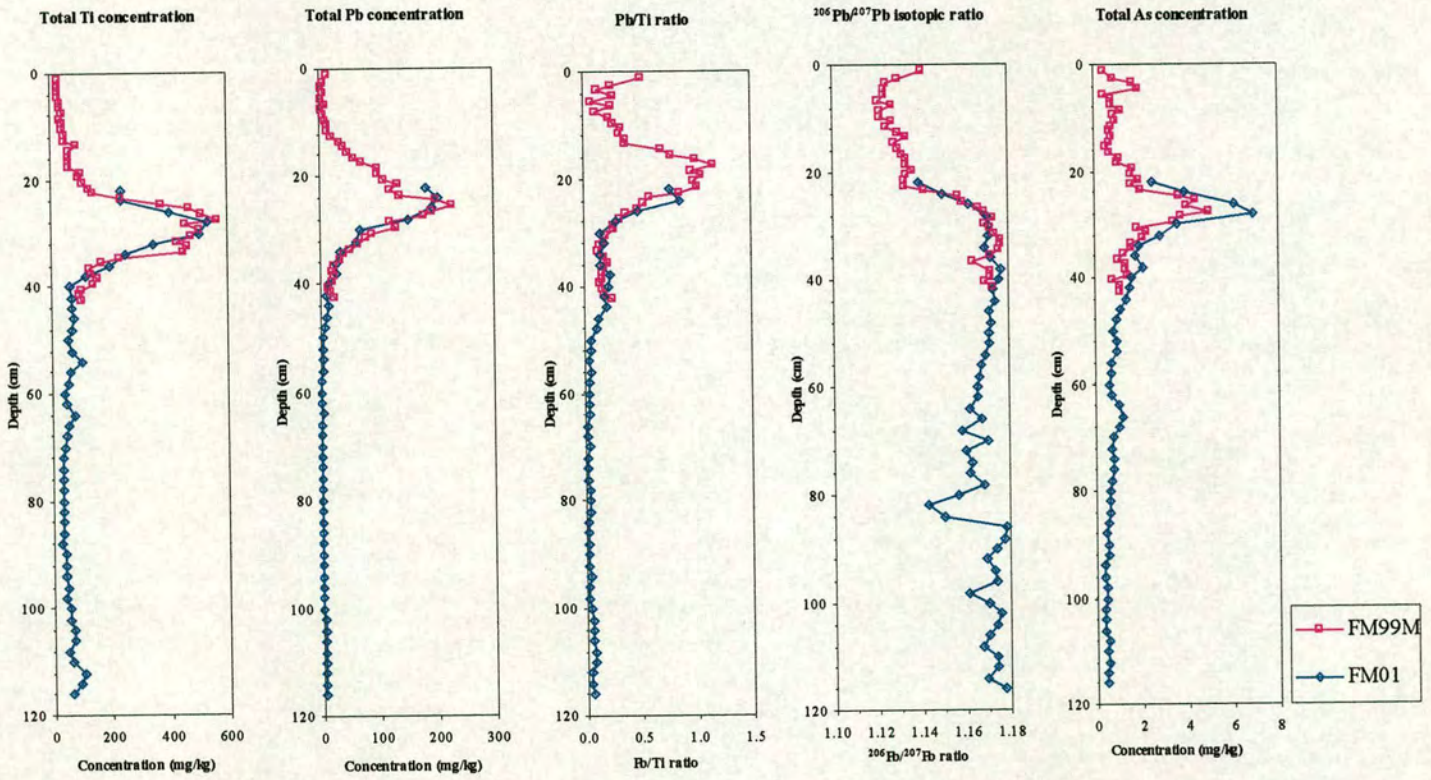


Figure 6.69 Ti, Pb concentration, Pb/Ti ratio, $^{206}Pb/^{207}Pb$ and As concentration versus depth (0 - 117 cm) in Flanders Moss peat cores.

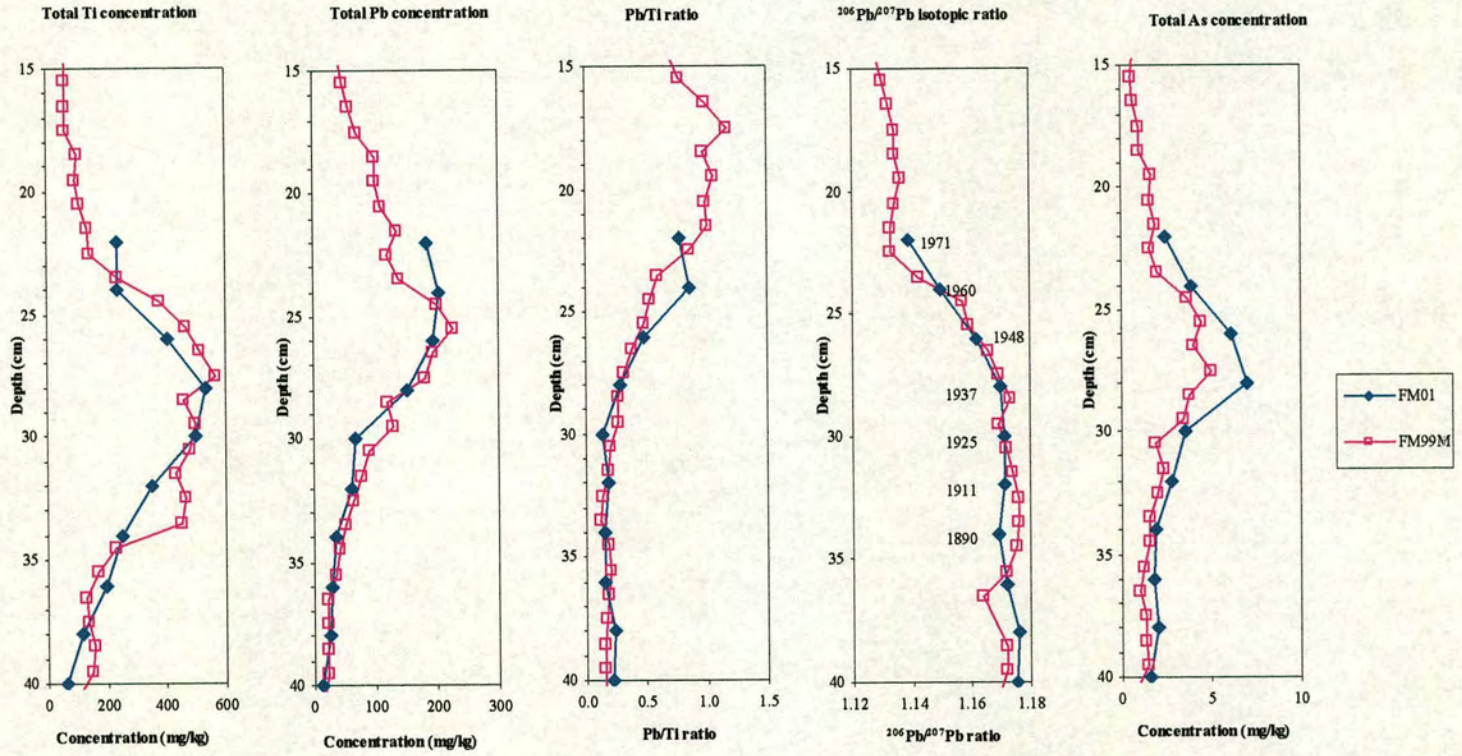


Figure 6.70 Vertical profiles of Ti concentration, Pb concentration, Pb/Ti ratio, $^{206}Pb/^{207}Pb$ and As concentration versus depth (15 - 40 cm) in Flanders Moss peat cores.

- the $^{206}Pb/^{207}Pb$ ratio, which is elevated above the mean, 1.161 ± 0.007, for 57 - 85 cm (mean Pb concentration 1.2 ± 0.4 mg/kg) lies predominantly in the 1.172 - 1.176 range
- the As concentration, which is elevated above the means, 0.40 to 0.82 mg/kg, for 57 - 101 cm, lies predominantly in the 1 - 2 mg/kg range

This would be consistent with the onset of the Industrial Revolution, as evidenced by the increasing concentration of Pb associated with a $^{206}Pb/^{207}Pb$ ratio typical of a mixture of indigenous sources of Pb (e.g. Pb mining and smelting at Wanlockhead/Leadhills ~ 1.170, coal burning 1.181 ± 0.011). The extent of coal burning, however, has not produced a significant increase in As concentration. The increase in Ti concentration may be associated with an increasing soil dust contribution, e.g. as a consequence of the clearing of land and agriculture.

From 35 to 30 cm (corresponding to 1876 to 1925):

- the Ti concentration increases quickly from ~ 200 to 450 - 500 mg/kg
- the Pb concentration increases from ~ 40 to ~ 100 mg/kg
- the Pb/Ti ratio remains fairly constant at ~ 0.15 - 0.20
- the $^{206}Pb/^{207}Pb$ ratio lies predominantly in the 1.170 - 1.176 range
- the As concentration increases from ~ 1.5 to ~ 3.5 mg/kg

The increase in As concentration would be consistent with increasing contributions from coal combustion. This would also be the case for Pb but contributions from other sources (including perhaps the onset of influence from imported Australian Pb of lower $^{206}Pb/^{207}Pb$ ratio ~ 1.04) may be reflected in the slight reduction in the $^{206}Pb/^{207}Pb$ ratio. The increase in Ti concentration may again be associated with an increasing soil dust contribution but, as discussed in Section 6.9.3, there may also be a contribution of Ti from coal combustion. The decrease in the mean As/Ti ratio (at a time of increasing As concentrations) to 0.0079 ± 0.0007 (FM01, 29-37 cm) from 0.017 ± 0.004 from 37 - 93 cm, however, suggests that the soil dust contribution of Ti has been significant.

From 30 to 25 cm (corresponding to 1925 to 1953):

- the Ti concentration stays high at ~ 450 - 550 mg/kg, with a maximum concentration at 27 - 28 cm
- the Pb concentration increases from ~ 100 to ~ 225 mg/kg
- the Pb/Ti ratio increases from ~ 0.2 to ~ 0.5
- the $^{206}Pb/^{207}Pb$ ratio decreases from ~ 1.17 to ~ 1.16
- the As concentration increases from ~ 3.5 to ~ 5 - 7 mg/kg at 27 - 29 cm, before declining to ~ 4 mg/kg

This zone of elevated As concentration would be consistent with major contributions from coal combustion. The increase in the mean As/Ti ratio (at a time of increasing As concentrations) to 0.0140 ± 0.0014 (FM01, 25 - 29 cm) from 0.0079 ± 0.0007 (FM01, 29 - 37 cm) and, for the FM99M core (where As concentrations are a little lower than in the FM01 core) to 0.0082 ± 0.0009 (FM99M, 25 - 30 cm) from 0.0048 ± 0.0013 (FM99M, 30 - 35 cm), however, suggests that the relative contribution of Ti from soil dust has been decreasing. This would also tie in with the increasing Pb/Ti ratio but contributions of Pb from a range of industrial sources (smelting, coal combustion) and, increasingly, from car-exhaust emissions are by now becoming highly significant. By the time (ca. 1953) of the maximum Pb concentration at ~ 25 cm, the $^{206}Pb/^{207}Pb$ ratio has decreased to ~ 1.16, indicative of the influence of Australian Pb of low $^{206}Pb/^{207}Pb$ ratio.

From 25 to 21 cm (corresponding to 1953 to 1976):

- the Ti concentration decreases from ~ 450 mg/kg to ~ 130 mg/kg,
- the Pb concentration decreases from ~ 200 to ~ 130 mg/kg
- the Pb/Ti ratio increases from ~ 0.5 to ~ 1.0
- the $^{206}Pb/^{207}Pb$ ratio decreases from ~ 1.16 to 1.133
- the As concentration decreases from ~ 4 to ~ 2 mg/kg

The trend in Ti concentration is consistent with decreasing contributions from soil dust (and coal combustion). The trend in As concentration is consistent with decreasing contributions from coal combustion but the maintenance of the higher As/Ti ratios of

0.0140 ± 0.0042 (FM01) and 0.0110 ± 0.0026 (FM99M) does suggest decreasing soil dust contributions of Ti as well. The less steep decline in Pb concentration, reflected in an increasing Pb/Ti ratio at a time of declining As and Ti concentrations, coupled with a marked shift in the $^{206}Pb/^{207}Pb$ ratio to lower values, indicates a change in the relative contributions from sources of indigenous Pb (e.g. coal, British ores) and Australian Pb (e.g. in petrol lead additives, leading to car-exhaust emissions of Pb of lower $^{206}Pb/^{207}Pb$ ratio), the latter becoming more noticeable.

Above 21 cm (corresponding to 1976 to ~ 2000):

- although there are data available for the top 21 cm of the FM99M core, there is no dating information for this part of the profile.

- for 21 to15 cm:
    - the Ti concentration decreases from ~ 130 mg/kg to ~ 60 mg/kg
    - the Pb concentration decreases from ~ 130 mg/kg to ~ 50 mg/kg
    - the Pb/Ti ratio increases slightly from ~ 1.0 to a maximum of 1.16 at 17 - 18 cm , before declining to ~ 0.8
    - the $^{206}Pb/^{207}Pb$ ratio lies predominantly between 1.132 and 1.136
    - the As concentration decreases from ~ 2 mg/kg to ~ 0.5 mg/kg.

  The trend in Ti concentration is consistent with decreasing contributions from soil dust. That the Pb/Ti ratio reaches a maximum at a time of decreasing Pb concentration and low $^{206}Pb/^{207}Pb$ ratio is consistent with the increasing relative contribution from a source of lower $^{206}Pb/^{207}Pb$ ratio, e.g. car-exhaust emissions. The decrease in As concentration is consistent with a decreasing input from coal combustion emissions.

- for 15 to 0 cm (Fig. 6.69)
    - the Ti concentration decreases from ~ 60 mg/kg to ~ 25 mg/kg
    - the Pb concentration decreases from ~ 50 mg/kg to <10 mg/kg

- the Pb/Ti ratio decreases from ~ 0.8 to < 0.2, although the surface value is slightly higher at ~ 0.5
- the $^{206}Pb/^{207}Pb$ ratio decreases from ~ 1.13 to ~ 1.12, before increasing to ~ 1.14 at the surface
- the As concentration is typically 0.4 - 0.9 mg/kg, although concentrations are 1.7 - 2.0 mg/kg from 3 - 5 cm.

In the absence of direct dating information for the FM99M core, it is more difficult to discuss these trends in terms of specific dates. It should also be remembered that the dating for the FM01 core was based on an estimate (25 years) of the number of years missing at the top. This estimate was associated with an uncertainty (± 1 s.d.) of ± 5 years. Furthermore, the upper parts of the FM99M core are more likely composed of living vegetation rather than decaying litter and peat and the application of an average peat accumulation rate derived from the FM01 core to the upper part of the FM99M core is not possible. But over the ~ 25-year period, it can be stated that the overall trend is consistent with decreasing input of soil dust, decreasing input of Pb but, on the basis of the $^{206}Pb/^{207}Pb$ data, with increasing relative contributions of car-exhaust emissions of Pb until the very topmost layers. There the reversal in trend of $^{206}Pb/^{207}Pb$ is consistent with the phasing out and complete withdrawal of Pb from petrol, the value of ~ 1.14 being close to those observed directly for the atmosphere (1.144 ± 0.017) and for *Sphagnum* moss (1.137 ± 0.010) collected in Scotland in the mid- to late 1990s (Farmer *et al.*, 2000, 2002). Prior to that, a mean value of 1.123 ± 0.003 for 6 - 10 cm is similar to that found for archival *Sphagnum* moss (mean 1.120 ± 0.018) in Scotland in the 1980s.

6.9.5.2 The "Roman" period

No dating (e.g. ^{14}C) is as yet available for the foot of the profile, i.e. 101 - 117 cm, where a region of elevated Pb concentration (mean 3.51 ± 0.45 mg/kg) and elevated Pb/Ti ratio (0.055 ± 0.014) has previously been identified (Table 6.19, Figs. 6.62, 6.64, 6.69). The mean $^{206}Pb/^{207}Pb$ ratio (1.173 ± 0.003) for 101 - 117 cm is also different from the mean

$^{206}Pb/^{207}Pb$ ratio (1.165 ± 0.009) for 57 - 101 cm, the region of lowest Pb concentration (mean 1.11 ± 0.43 mg/kg). If these latter values are, for the moment, taken to represent "natural" Pb, then the mean $^{206}Pb/^{207}Pb$ ratio for "anthropogenic" Pb in the 101 - 117 cm zone is 1.176 ± 0.005. A slightly longer sister core collected from Flanders Moss showed a mean Pb concentration of 1.64 ± 0.25 mg/kg and a mean $^{206}Pb/^{207}Pb$ ratio of 1.165 ± 0.004 for sections below the putative Roman peak. The mean Ti concentration was 42 ± 5 mg/kg, with a mean Pb/Ti ratio of 0.039 ± 0.006. Use of the mean Pb and $^{206}Pb/^{207}Pb$ values for the bottom sections from this other core yielded a mean $^{206}Pb/^{207}Pb$ value of 1.180 ± 0.008 for the anthropogenic Pb in the FM01 core. These values of 1.176 ± 0.005 and 1.180 ± 0.008 are similar to that reported for the anthropogenic Pb detected in Greenland ice for the Roman period, during which there was considerable mining and smelting of various European Pb ores (Rosman *et al.*, 1997). Similarly, Shotyk *et al.* (1998) found a Roman Pb peak, with characteristic Pb isotopic signature, at a similar depth in a ^{14}C-dated Swiss ombrotrophic peat bog, as have Le Roux *et al.* (2004) in an English bog. Thus it seems likely that 101 - 117 cm represents at least part of the Roman period, although confirmation must await the ^{14}C dating of the other core.

6.9.5.3 The intermediate years – from the Romans to the industrial period

From 101 to 57 cm (Table 6.19, Figs. 6.62, 6.64, 6.69):

- the Ti concentration is relatively constant, with a mean of 41.5 ± 10.1 mg/kg (93 - 101 cm, 46.3 ± 5.1 mg/kg; 71 - 93 cm, 34.5 ± 3.9 mg/kg; 57 - 71 cm, 49.7 ± 11.7 mg/kg)
- the Pb concentration is relatively constant, with a mean of 1.11 ± 0.43 mg/kg (93 - 101 cm, 1.38 ± 0.25 mg/kg; 71 - 93 cm, 0.78 ± 0.16 mg/kg; 57 - 71 cm, 1.50 ± 0.37 mg/kg)
- the Pb/Ti ratio is relatively constant, with a mean of 0.027 ± 0.006 mg/kg (93 - 101 cm, 0.030 ± 0.004; 71 - 93 cm, 0.023 ± 0.005; 57 - 71 cm, 0.030 ± 0.006)
- the $^{206}Pb/^{207}Pb$ ratio, with an overall mean value of 1.165 ± 0.009 from 57 - 101 cm, varies from 1.170 ± 0.006 (93 - 101 cm) to 1.175 ± 0.004 (85 - 93 cm) to 1.157 ± 0.009 (71 - 85 cm) and 1.165 ± 0.004 (57 - 71 cm)

- the As concentration increases slightly from 0.40 ± 0.05 mg/kg (93 - 101 cm) to 0.59 ± 0.11 mg/kg (71 - 93 cm) and 0.82 ± 0.22 mg/kg (57 - 71 cm)

This is certainly the region of the profile with least anthropogenic influence but that doesn't mean that it can necessarily be ruled out, given the known renaissance of mining and smelting in Europe in mediaeval times and, from the data above, the enhancement of even the low Pb/Ti ratio relative to the corresponding crustal value. There is no obvious explanation of the low $^{206}Pb/^{207}Pb$ values of 1.143 – 1.156 from 79 – 85 cm, especially as the Pb concentrations of 0.6 – 1.0 mg/kg were not noticeably different from the rest of 71 – 93 cm (0.5 – 1.0 mg/kg).

From 57 to 40 cm:

- the Ti concentration increases from ~ 50 to ~ 100 mg/kg
- the Pb concentration increases from 1 - 2 to ~ 15 mg/kg
- the Pb/Ti ratio increases from ~ 0.03 to ~ 0.2
- the $^{206}Pb/^{207}Pb$ ratio increases from ~ 1.165 to ~ 1.175
- the As concentration increases from ~ 0.8 to ~ 1.5 mg/kg

Again, no dates are yet available for this period, but the above data for the 40 - 57 cm region show clear anthropogenic influence and represent either the pre-industrial period or the early stages of the industrial period, usually taken to begin at ca. 1760 in Scotland. The enhancement in Pb relative to that in Ti is indicative of anthropogenic influence, for example from local mining and smelting.

6.9.5.4 Inventories, fluxes and sources of Pb

The inventories of Pb for the individual periods and depth zones of the peat profile are summarised in Table 6.20.

Table 6.20 Summary of Pb inventories for different depth zones of Flanders Moss peat.

Depth (cm)	Date	FM99M Pb ($g\ m^{-2}$)	FM01 Pb ($g\ m^{-2}$)	FM99M Dry wt. ($g\ cm^{-2}$)	FM01 Dry wt. ($g\ cm^{-2}$)
0-15	?-1999	0.136	-	0.887	-
15-21	1976-?	0.604	-	0.707	-
21-25	1953-1976	0.459	0.708	0.301	0.364
25-30	1925-1953	1.367	1.149	0.811	0.757
30-35	1876-1925	0.412	0.303	0.634	0.667
35-40		0.118	0.137	0.462	0.551
40-57		(0.048)	0.099	(0.255)	1.385
57-71			0.014		0.911
71-93			0.012		1.574
93-101			0.009		0.650
101-117			0.044		1.242

With the possible exception of the Pb inventory for 21 - 25 cm, there is good agreement between the inventories for both Pb and dry weight between the FM99M and FM01 cores. If the Pb inventory (0.164 $g\ m^{-2}$) for the 20 - 21 cm section of the FM99M core is included with the 21 - 25 cm zone instead of the 15 - 21 cm zone, the revised inventory for the 1953 - 1976 period for FM99M, 0.623 $g\ m^{-2}$, is much closer to the value (0.708 $g\ m^{-2}$) for the FM01 core. The revised value for the 15-21 cm zone is then 0.440 $g\ m^{-2}$, and that for the 0-21 cm zone is 0.576 $g\ m^{-2}$.

For the ^{210}Pb-dated portion of the peat profile, i.e. from 21 to 35 cm, corresponding to 1876 - 1976, the calculated average flux of Pb deposited from the atmosphere for each time period is plotted along with the corresponding $^{206}Pb/^{207}Pb$ ratio in Fig. 6.71. The highest Pb flux of 57.0 mg m^{-2} y^{-1} is associated with the 1943 - 1953 period. This is similar both in magnitude and date to the maximum anthropogenic Pb flux calculated from sediment studies on the southern basin of nearby Loch Lomond and, indeed, for other lake sediments in Scotland (Eades *et al.*, 2002).

There is also some evidence from Scottish lake sediment and archival moss data (Section 6.9.5.1) to support the observed temporal trend in $^{206}Pb/^{207}Pb$ (Eades *et al.*, 2002; Farmer *et al.*, 2002), although the onset of the major shift in $^{206}Pb/^{207}Pb$ from a value of ~ 1.17 could perhaps be considered to have occurred some 10 years later in the Flanders Moss peat. To bring these records into line, the "missing" material at the top of the FM01 core, would have to correspond to 35 years rather than 25 years. Bearing in mind the ± 1 standard deviation of ± 5 years on the estimate of 25 years, this would be not inconceivable. It would, however, shift the date of maximum Pb flux some 10 years earlier to ca. 1940.

Retaining the dating based on a loss of material corresponding to just 25 years, however, yields the plot of Pb and As fluxes with time in Fig. 6.72. This demonstrates a decrease in As flux relative to Pb flux with time, reflecting both an absolute decline in coal combustion (and the As flux) and a decline in coal combustion relative to other sources of Pb (e.g. car-exhaust emissions).

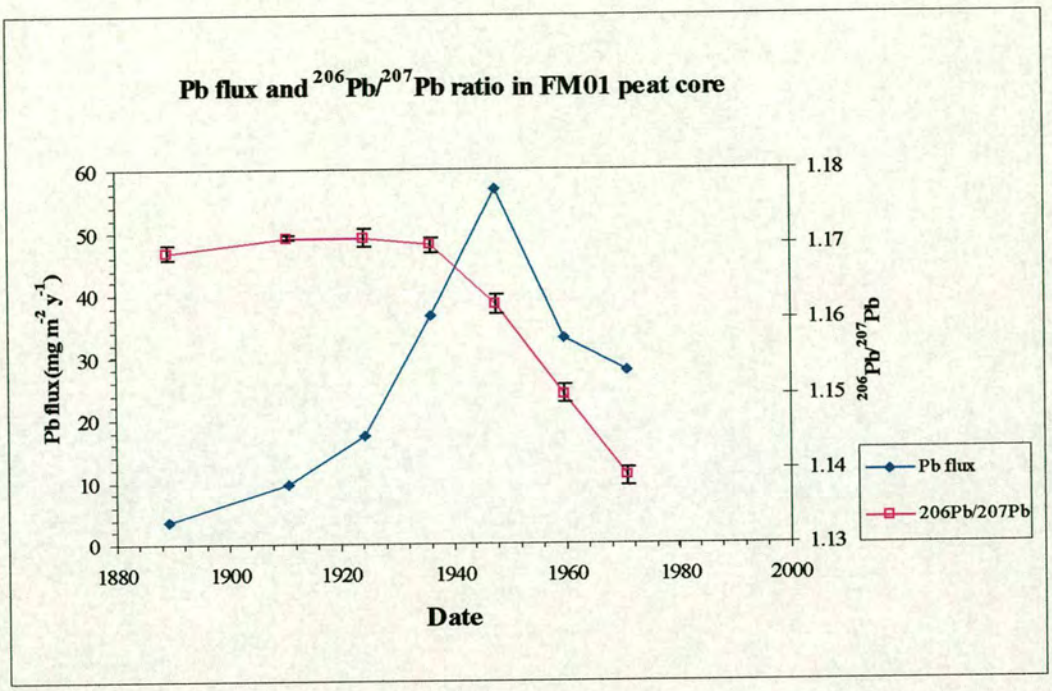


Figure 6.71 The calculated average flux of Pb deposited from the atmosphere and the corresponding $^{206}Pb/^{207}Pb$ ratio for time periods between 1876 and 1976 at Flanders Moss.

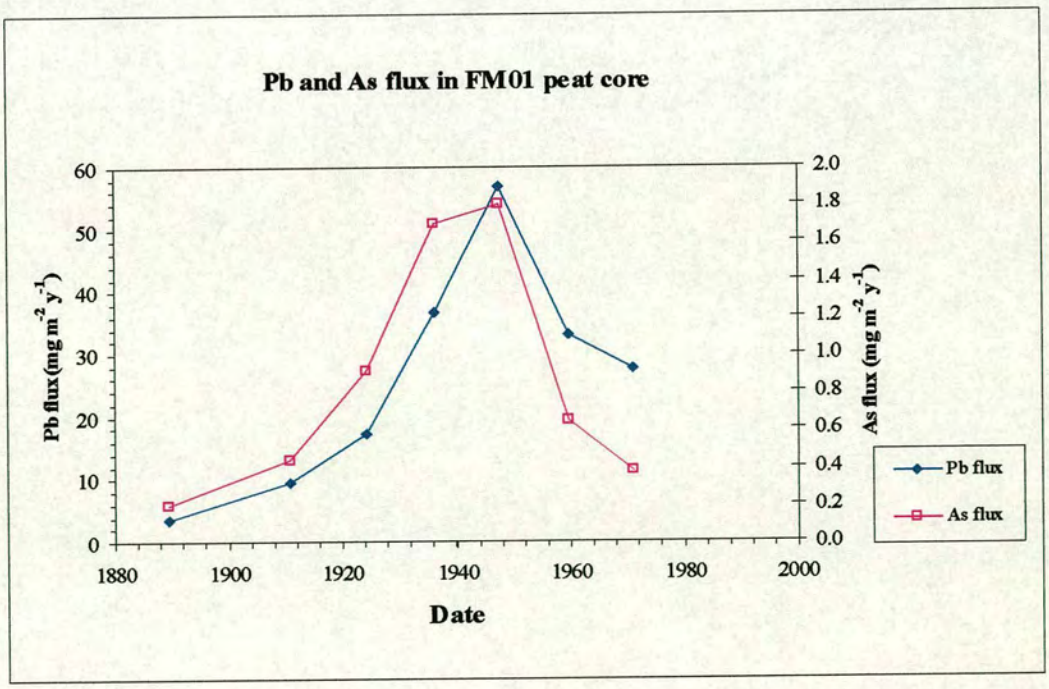


Figure 6.72 The calculated average flux of Pb and As deposited from the atmosphere for time periods between 1876 and 1976 at Flanders Moss.

For anthropogenic Pb (with isotopic ratio $^{206}Pb/^{207}Pb_{anthrop}$) to which there are contributions from two components (e.g. $^{206}Pb/^{207}Pb_{petrol}$ and $^{206}Pb/^{207}Pb_{other}$), source apportionment calculations can be carried out using the following type of equation:

$$Pb_{petrol}(\%) = \frac{(^{206}Pb/^{207}Pb_{other} - ^{206}Pb/^{207}Pb_{anthrop})}{(^{206}Pb/^{207}Pb_{other} - ^{206}Pb/^{207}Pb_{petrol})} \times 100$$

This approach does have weaknesses, such as the possible variation with time of the $^{206}Pb/^{207}Pb$ ratio of individual emission sources. Also, the potential uniqueness of the emission source Pb isotopic signature, (e.g. $^{206}Pb/^{207}Pb_{petrol}$), defined in terms of the geochemical origins of the Pb in the parent material (e.g. ore), may not have been restricted to one particular emission source in terms of the mode or pathway of release to the atmosphere (cf. smelting of ore). Nevertheless, it is instructive to carry out source apportionment calculations for anthropogenic Pb using the post-1940 $^{206}Pb/^{207}Pb$ values obtained in FM01 as $^{206}Pb/^{207}Pb_{anthrop}$ (i.e. ignoring any slight "natural" contribution) along with a $^{206}Pb/^{207}Pb_{other}$ value of 1.17 for overall industrial contributions, which incorporate those of coal (1.181 ± 0.011) combustion (Farmer *et al.*, 1999), and a range for $^{206}Pb/^{207}Pb_{petrol}$ values of 1.06-1.09 (Sugden *et al.*, 1993; Farmer *et al.*, 2000). The calculated contributions from petrol Pb range from 7 - 10% for 1943 - 1953, 18 - 25% for 1953 - 1967, and 28 - 39% for 1967 - 1976. Thus, over the period 1876 - 1976, petrol Pb would have contributed no more than ~ 13 % of the FM01 Pb inventory of 2.16 g m^{-2} for that period, confirming the importance of other sources to the past atmospheric deposition of Pb in Scotland. For the period since 1976, the minimum $^{206}Pb/^{207}Pb_{anthrop}$ value of 1.121 observed a few cm below the surface of the FM99M core yields a range of 45 – 61 % for petrol Pb, while the FM99M surface $^{206}Pb/^{207}Pb_{anthrop}$ value of 1.141 corresponds to a range of 26 – 36 %. These ranges are broadly in line with the decline in calculated contribution of car-exhaust emissions of Pb from leaded petrol to atmospheric Pb in Scotland from the late 1980s/early 1990s until the late 1990s, based on rainwater measurements, from 53-61% to 32 – 45 % (Farmer *et al.*, 2000).

6.9.6 Conclusions

The principal conclusions arising from the application of analytical methods and quality control procedures to two Flanders Moss peat cores collected by different methods and at different times were as follows:

- acid-extractable concentrations were lower than total concentrations for some major, "conservative" elements (e.g. Al, Ti) and some trace elements (e.g. Cr, Ni, V), confirming the importance of total digestion methods and the use of the certified reference material
- a comparison of profiles of elemental concentrations versus depth for the two peat cores collected by different methods revealed an offset (~ 21 cm) between the two cores, at least partially attributable to a loss of material (as reflected in a ^{210}Pb deficit) from the top of one of the cores during sampling
- differences in the peat profiles of various elements deposited from the atmosphere were attributed to nutrient uptake and recycling (e.g. Mn, P, Zn, S), historical variations in the anthropogenic release of heavy (e.g. Pb, As, Cd, Cr, Cu, V) and other (e.g. S) elements to the atmosphere since the onset of the Industrial Revolution, variations in soil-dust-related inputs (and, in recent times, possible industrial contributions) of "conservative" elements (e.g. Al, Ti) to the atmosphere, post-depositional remobilisation and redistribution of redox-sensitive (e.g. Fe) and associated (e.g. P) elements and the possible influence of sulphide formation (e.g. on Zn) under the conditions pertaining in the bog, and, for Pb, the influence (suggested by a concentration peak at a depth of ~ 1 m) of emissions from the smelting of Pb ores during the Roman Empire
- on the basis of ^{210}Pb dating, the stable Pb isotopic composition (e.g. $^{206}Pb/^{207}Pb$) and a comparison of Pb and As profiles, variations in the relative importance of contributions of Pb from different sources (e.g. smelting of indigenous Pb ores, coal combustion, Australian-Pb-influenced car-exhaust emissions) since the 1870s were discerned and assessed, the importance of sources other than those related to petrol Pb being confirmed so far as the anthropogenic Pb burden of the Scottish environment is concerned.

Chapter 7
Conclusions

7.1 Summary of conclusions of thesis

Two microwave-assisted digestion methods, the adapted USEPA method 3051 (HNO_3), which represents acid-extractable concentrations, and the adapted USEPA method 3052 (HNO_3/HF), which provides total elemental concentrations, have been proposed after a series of investigations of various digestion methods for peat material in Chapter 3. They are named (1) the adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat and (2) adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat. The full details of these digestion methods are given in Appendix A.

The two proposed digestion methods for peat material were applied to the determination of inorganic elements in a Flanders Moss peat core collected in 1999. From this experiment we can conclude that both total and acid-extractable digestion methods generate similarly shaped vertical profiles of elemental concentrations in this Flanders Moss ombrotrophic peat core. However, total concentrations of some major elements such as Al and Ti are clearly higher than acid-extractable concentrations. In summary, it is necessary to use HF in the digestion of peat material to achieve total elemental concentrations, especially for major elements and some trace elements such as Cr and V. Also, it was discovered that peat from a depth of ~ 20 - 40 cm should be collected from Flanders Moss in order to have reasonably high elemental concentrations in the intended ombrotrophic peat reference material.

The ombrotrophic peat bog (low-ash) reference material was successfully developed. Preparation of the candidate peat reference material was achieved with help from the Macaulay Institute, Aberdeen. It was named "NIMT/UOE/FM/001". Homogeneity and stability testing of the candidate material, carried out at the University of Edinburgh, proved that the material was homogeneous and stable during the period of study. Certification of the peat bog reference material was achieved by an international inter-laboratory comparison, fourteen laboratories from nine countries participating in the exercise. Ten laboratories supplied data for acid-extractable (HNO_3, HNO_3/HCl, HNO_3/$HClO_4$) concentrations and seven for total (HNO_3/HF,

HNO_3/HBF_4, $HNO_3/H_2O_2/HF$) concentrations, using a range of digestion conditions and a variety of analytical techniques (AAS, ICP-OES, ICP-MS), including, in the case of one laboratory, XRF analysis of the solid phase, and, in two others, thermal decomposition AAS for Hg. After subsequent rigorous statistical tests to reject outliers, the certified (coverage factor of 2) or information-only (± 1 S.D.) values, as appropriate, for acid-extractable and total Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, P, Pb, S, Ti, V and Zn concentrations were calculated, as reported in Table 4.10 of Chapter 4. The certificate was issued, as given in Appendix F.

In addition to elemental concentration data, information on Pb isotopic composition was provided by three laboratories. Reported mean values of 1.1766 ± 0.0008, 1.1759 ± 0.0006, and 1.1765 ± 0.0003, yielded an overall information value of 1.176 for the $^{206}Pb/^{207}Pb$ ratio.

Isotope dilution mass spectrometry (IDMS) was applied to the determination of Pb in the peat reference material "NIMT/UOE/FM/001". The Pb concentrations determined by IDMS analysis of both a digest solution and the solid peat sample itself were close to the certified value in the inter-laboratory comparison (Table 5.11, Chapter 5). The uncertainties of the Pb concentrations were calculated according to the guidelines of the EURACHEM/CITAC Guide Quantifying Uncertainty in Analytical Measurement. The uncertainty assigned to the Pb concentration value obtained from the digest solution was lower than that for the solid peat material. The major advantage of IDMS applied to the solid peat material is that the uncertainties arising during the digestion and analytical procedures were included throughout the process. Any contamination and subsequent losses of Pb during the analytical procedure do not affect the result obtained by IDMS on solid peat material. From this study, it has been established that the application of the IDMS method to the determination of Pb in the solid peat reference material provides accurate analytical results.

Chapter 6 focused on the generation and interpretation of vertical profiles of inorganic elements in Flanders Moss peat cores. The principal conclusions arising from the application of analytical methods and quality control procedures to two Flanders Moss peat cores collected by different methods and at different times were as follows:

- acid-extractable concentrations were lower than total concentrations for some major, "conservative" elements (e.g. Al, Ti) and some trace elements (e.g. Cr, Ni, V), confirming the importance of total digestion methods and the use of the certified reference material
- a comparison of profiles of elemental concentrations versus depth for the two peat cores collected by different methods revealed an offset (~ 21 cm) between the two cores, at least partially attributable to a loss of material (as reflected in a ^{210}Pb deficit) from the top of one of the cores during sampling
- differences in the peat profiles of various elements deposited from the atmosphere were attributed to:
    - nutrient uptake and recycling (e.g. Mn, P, Zn, S),
    - historical variations in the anthropogenic release of heavy (e.g. Pb, As, Cd, Cr, Cu, V) and other (e.g. S) elements to the atmosphere since the onset of the Industrial Revolution,
    - variations in soil-dust-related inputs (and, in recent times, possible industrial contributions) of "conservative" elements (e.g. Al, Ti) to the atmosphere,
    - post-depositional remobilisation and redistribution of redox-sensitive (e.g. Fe) and associated (e.g. P) elements and the possible influence of sulphide formation (e.g. on Zn) under the conditions pertaining in the bog, and,
    - for Pb, the influence (suggested by a concentration peak at a depth of ~ 1 m) of emissions from the smelting of Pb ores during the Roman Empire
- on the basis of ^{210}Pb dating, the stable Pb isotopic composition (e.g. ^{206}Pb/^{207}Pb) and a comparison of Pb and As profiles, variations in the relative importance of contributions of Pb from different sources (e.g. smelting of indigenous Pb ores, coal combustion, Australian-Pb-influenced car-exhaust emissions) since the 1870s were discerned and assessed, the importance of sources other than those related to petrol Pb being confirmed so far as the anthropogenic Pb burden of the Scottish environment is concerned.

Overall, the digestion methods developed and tested in this study offer a suitable standard digestion protocol for peat material. The ombrotrophic peat bog certified reference material developed in this project will be valuable to all laboratories engaged in studies of past atmospheric metal deposition using peat bogs as archives. The accurate determination of elemental vertical profiles in two Flanders Moss peat cores adds significantly to understanding of past atmospheric metal deposition in Scotland.

7.2 Further research

The following are suggested as areas for further research.

1. Certification of more elements in the ombrotrophic peat bog reference material.
2. Investigation of the stability of the ombrotrophic peat bog reference material over a longer period of time.
3. Investigation of the effects of different types of corers on the resultant elemental profiles obtained in peat cores.
4. Investigation of the influence of topography and vegetation type on spatial and temporal variations in elemental concentrations and inventories in ombrotrophic peat bogs.
5. Use of a larger diameter and longer peat corer to collect more material for readier provision of radionuclide dating information.
6. Investigation of the validity of the enrichment factor approach to the assessment of anthropogenic heavy element contamination via the use of normalisation to conservative elements such as Al, Ti, Sc, Zr in background (at greater depth in peat) and crustal material.

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Appendix A

Adapted USEPA Methods for the Determination of Inorganic Elements in Peat

1. The adapted USEPA method 3051 protocol: microwave-assisted HNO_3 digestion of peat
2. The adapted USEPA method 3052 protocol: microwave-assisted HF/HNO_3 digestion of peat

Adapted USEPA Method 3051 Protocol: Microwave-assisted HNO_3 digestion of peat (total-recoverable digestion method)

1.0 Scope and Application

1.1 This digestion method according to the USEPA Method 3051 is adopted as the harmonised extraction protocol for the certification campaign of the ombrotrophic peat bog candidate reference material. This method provides the extractable content of elements in the sample.
1.2 This procedure is modified from the USEPA Method 3051 by ashing samples in the muffle furnace at 450°C to remove organic material in peat samples before commencing the digestion process. This method is not suitable for determination of Hg.
1.3 This method is applicable to the microwave-assisted acid digestion of peat sample for the following elements:

Aluminium, Iron, Sodium, Calcium, Lead, Nickel, Chromium, Magnesium, Manganese, Vanadium, Titanium, Copper, Sulfur, Phosphorus, and Zinc

1.4 This method is intended to provide a rapid multi-element acid digestion prior to analysis. Digests produced by this method are suitable for analysis by flame atomic absorption (FAAS), graphite furnace atomic absorption (GFAAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS).

2.0 Summary of Method

2.1 A representative sample of up to 0.25 g (the initial weight) is digested in 10 ml of concentrated nitric acid for 10 mins using microwave heating with a suitable laboratory microwave unit. The sample and acid are placed in a fluorocarbon (PFA or TFM) microwave vessel. The vessel is capped and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analysed by the appropriate SW-846 method (U.S. Environmental Protection Agency, 1986).

3.0 Warning & Safety Precautions

3.1 Concentrated Nitric Acid (HNO_3) is irritant, harmful and corrosive if inhaled or contact made with eyes or skin. Skin contact with concentrated nitric acid should be avoided.
3.2 The whole procedure (except weighing) should be carried out in a fume cupboard. Lab coat, safety glasses and gloves should be worn all times.
3.3 Great care should be taken when pouring concentrated acids.

4.0 Apparatus and Materials

4.1 Microwave apparatus requirements.
4.1.1 The microwave unit provides programmable power with a minimum of 574 W, which can be programmed to within ±10 W of the required power. Typical units provide a nominal 600 W to 1200 W of power. Pressure, or especially temperature, monitoring and control of the microwave unit are desirable.
4.1.2 The microwave unit cavity is corrosion-resistant and well ventilated.
4.1.3 All electronics are protected against corrosion for safe operation.

4.1.4 The system requires fluorocarbon (PFA or TFM) digestion vessels (120 ml capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).
4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.
4.2 Volumetric graduated flask, 25 or 50 ml capacity or equivalent.
4.3 Filter paper, qualitative or equivalent.
4.4 Filter funnel, glass or disposable polypropylene.
4.5 Analytical balance, 300 g capacity, and minimum ±0.001 g.

5.0 Reagents

5.1 All reagents should be of appropriate purity or high purity (acids for example, should be sub-boiling distilled where possible) to minimise the blank levels due to elemental contamination.
5.2 Reagent water shall be interference free. All references to water in the method refer to reagent water.

6.0 Procedure

6.1 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. All digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid (but not boil) for a minimum of two hours followed with hot (1:1) nitric acid (but not boil) for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 2 M) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment.
6.2 Sample Digestion
6.2.1 Weigh approximately 0.25 g of a well-mixed peat sample to the nearest 0.001 g, then place in a muffle furnace for four hours at 100°C, and for a further four hours at 450°C.
6.2.2 Transfer the sample into the fluorocarbon sample vessel equipped with a single-ported cap and a pressure relief valve.
6.2.3 Add 10 ± 0.1 ml concentrated nitric acid in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lbs (16 N-m) or according to the unit manufacturer's directions. Place the vessels in the microwave carousel.
6.2.4 Properly place the carousel in the microwave unit according to the manufacturer's recommended specifications and, if used, connect the pressure vessels to the central overflow vessel with PFA-fluorocarbon tubes.
6.2.5 Irradiate each group of sample vessels for 10 minutes. The temperature of each sample should rise to 175°C in less than 5.5 minutes and remain between 170-180°C for the balance of the 10 minutes irradiation period.
6.2.6 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave unit.
6.2.7 When the vessels have cooled to room temperature, carefully uncap and vent each vessel in a fume hood. Transfer the sample to an acid-cleaned beaker. If the digested sample contains undigested particulates, which may clog nebulisers or interfere with injection of the sample into the instrument, the sample may be filtered.
6.2.7.1 Filtering: The filtering apparatus must be thoroughly cleaned. Filter the sample through qualitative filter paper into a second acid-cleaned container.
6.2.8 Evaporate the solutions down to approximately 1 ml on a hotplate.

6.2.9 Dilute the digest to a known volume with 2% v/v nitric acid. The digest is now ready for analysis for elements of interest using the appropriate SW-846 method (U.S. Environmental Protection Agency, 1986).

7.0 Calculation

The final concentration of metals in peat sample (C) was calculated from:

$$C = \frac{C_0 \cdot V_L}{m_{Sample}} \text{ mg/kg}$$

where:

C_0	=	Concentration of metal in the digested solution subtracted by concentration in sample blank (mg/l)
V_L	=	Final volume of extract (l)
m_{Sample}	=	Dry weight of the investigated sub-sample (kg) (Dry weight should be determined on non-analysed aliquots oven-dried at 105 °C until the constant weight was obtained.)

8.0 Quality Control

8.1 Spiked samples or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number of samples.
8.2 At least one sample blank should be carried out in every batch of sample preparation.

9.0 References

1. *Method 3051 Microwave assisted acid digestion of sediments, sludges, soils, and oils*, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1994.
2 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed;* U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1986; SW-846.
3. ASTM Standard: D 2974-87, Standard Test Method for Moisture, Ash, and Organic Matter of Peat materials, 1993, 479-480.

Adapted USEPA Method 3052 Protocol: Microwave-assisted HF/HNO_3 digestion of peat (total-total digestion method)

1.0 Scope and Application

1.1 This digestion method according to the USEPA Method 3052 is adopted as the harmonised extraction protocol for the certification campaign of the ombrotrophic peat bog candidate reference material.

1.2 This procedure is modified from the USEPA Method 3052 by ashing samples in the muffle furnace at 450°C to remove organic material in peat samples before commencing the digestion process. This method is not suitable for determination of Hg.

1.3 This method is intended to provide total-total acid digestion of peat samples. This method is applicable for the following elements:

Aluminium, Iron, Sodium, Calcium, Lead, Nickel, Chromium, Magnesium, Manganese, Vanadium, Titanium, Copper, Sulfur, Phosphorus, and Zinc

1.4 This method is provided as a rapid multi-element, microwave-assisted acid digestion prior to analysis. Digests produced by this method are suitable for analysis by flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS) and other elemental analysis techniques where applicable.

2.0 Summary of Method

2.1 A representative sample of up to 0.25 g (the initial weight) is digested in 9 ml of concentrated nitric acid and 0.5 ml hydrofluoric acid for about 15 minutes using microwave heating with a suitable laboratory microwave system. The sample and acid are placed in suitably inert polymeric microwave vessels. The vessel is sealed and heated in the microwave system. The temperature profile is specified to permit specific reactions and incorporates reaching 180 ± 5°C in approximately less than 5.5 minutes and remaining at 180 ± 5°C or 9.5 minutes for the completion of specific reactions.

3.0 Warning & Safety Precautions

3.1 Concentrated Hydrofluoric Acid (HF) causes severe, painful burn on contact with all body tissue.

3.2 Concentrated Nitric Acid (HNO_3) is irritant, harmful, and corrosive if inhaled or contact made with eyes or skin.

3.3 The whole procedure (except weighing) should be carried out in a fume cupboard.

3.4 Lab coat, safety glasses and gloves should be worn all times and must not at any time permit a solution containing hydrofluoric acid to come in contact with skin. Great care should be taken when pouring concentrated acids.

3.5 If hydrofluoric acid makes contact with skin, neutralise with anhydrous sodium carbonate or calcium gluconate first. Then consult a doctor as soon as possible.

3.6 The removal of excess hydrofluoric acid, which is capable of dissolving silicates, or the use of specialised non-glass components may be required during instrumental analysis.

4.0 Apparatus and materials

4.1 Microwave apparatus requirements.
4.1.1 The temperature performance requirements necessitate that the microwave decomposition system senses the temperature to within ±2.5°C and automatically adjusts the microwave field output power within 2 seconds of sensing. Temperature sensors should be accurate to ±2°C (including the final reaction temperature of 180°C).
4.1.2 The microwave unit cavity is corrosion-resistant and well-ventilated. All electronics are protected against corrosion for safe operation.
4.1.3 The method requires essentially microwave-transparent and reagent-resistant suitably inert polymeric materials (examples are PFA or TFM suitably inert polymeric polymers) to contain acids and samples. The internal volume of the vessels should be at least 45 ml, capable of withstanding pressures of at least 30 atm (30 bar or 435 psi), and capable of controlled pressure relief.
4.1.4 A rotating turntable is employed to ensure homogeneous distribution of microwave radiation within most systems. The speed of the turntable should be a minimum of 3 rpm.
4.2 Volumetric ware, volumetric flasks, and graduated cylinders, 25 and 50 ml capacity or equivalent.
4.3 Filter paper, qualitative or equivalent.
4.4 Filter funnel, polypropylene, polyethylene or equivalent.
4.5 Analytical balance, of appropriate capacity, with a ±0.001 g or appropriate precision for the weighing of the sample.

5.0 Reagents

5.1 All reagents should be of appropriate purity or high purity (acids for example, should be sub-boiling distilled where possible) to minimise the blank levels due to elemental contamination. All references to water in the method refer to reagent water.

6.0 Procedure

6.1 Temperature control of closed vessel microwave instruments provides the main feedback control performance mechanism for the method. Control requires a temperature sensor in one or more vessels during the entire decomposition. The microwave decomposition system should sense the temperature to within ±2.5°C and permit adjustment of the microwave output power within 2 seconds.
6.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. All digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid (but not boil) for a minimum of two hours followed by hot (1:1) nitric acid (but not boil) for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware (not used with hydrofluoric acid) and storage containers should be cleaned by leaching with more dilute acids (approximately 2 M) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment.
6.3 Sample Digestion
6.3.1 Weigh approximately 0.25 g of a well-mixed peat sample to the nearest 0.001 g, then place in a muffle furnace for four hours at 100°C, and for a further four hours at 450°C.
6.3.2 Transfer the sample into the fluorocarbon sample vessel equipped with a single-ported cap and a pressure relief valve.
6.3.3 Add 9 ± 0.1 ml concentrated nitric acid and 0.5 ± 0.1 ml concentrated hydrofluoric acid to the vessel in a fume hood.

6.3.4 Seal the vessel according to the manufacturer's directions. Properly place the vessel in the microwave system according to the manufacturer's recommended specifications and connect appropriate temperature and pressure sensors to vessels according to manufacturer's specifications.
6.3.5 Irradiate each group of sample vessels for 10 minutes. The temperature of each sample should rise to 180°C in less than 5.5 minutes and remain at 180 ± 5°C for the balance of the 9.5 minutes irradiation period.
6.3.6 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave unit.
6.3.7 When the vessels have cooled to room temperature, carefully uncap and vent each vessel in a fume hood. Transfer the sample to an acid-cleaned Teflon beaker. If the digested sample contains undigested particles, which may clog nebulisers or interfere with injection of the sample into the instrument, the sample may be filtered.
6.3.7.1 Filtering: The filtering apparatus must be thoroughly cleaned. Filter the sample through qualitative filter paper into a second acid-cleaned container.
6.3.8 Evaporate the solutions down to approximately 1 ml on a hotplate.
6.3.9 Dilute the digest to a known volume with 2% v/v nitric acid. The digest is now ready for analysis for elements of interest using the appropriate SW-846 method (U.S. Environmental Protection Agency, 1986).

7.0 Calculation

The final concentration of metals in peat sample (C) was calculated from:

$$C = \frac{C_0 \cdot V_L}{m_{Sample}} \text{ mg/kg}$$

where:

C_0	=	Concentration of metal in the digested solution subtracted by concentration in sample blank (mg/l)
V_L	=	Final volume of extract (l)
m_{Sample}	=	Dry weight of the investigated sub-sample (kg) (Dry weight should be determined on non-analysed aliquots oven-dried at 105 °C until the constant weight was obtained.)

8.0 Quality Control

8.1 Spiked samples or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number of samples.
8.2 At least one sample blank should be carried out in every batch of sample preparation.

9.0 References

1. *Method 3052 Microwave assisted acid digestion of siliceous and organically based matrices,* U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1996.
2 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed;* U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1986; SW-846.
3. ASTM Standard: D 2974-87, Standard Test Method for Moisture, Ash, and Organic Matter of Peat materials, 1993, 479-480.

Appendix B

Preliminary Homogeneity Study of Bulk Candidate Ombrotrophic Peat Bog Reference Material

Raw data for total elemental concentration (mg/kg), Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, P, S, Ti, V, and Zn, (dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat) in the preliminary homogeneity testing of the candidate ombrotrophic peat (low ash) reference material are shown.

Table 1 Data for total Al concentration (mg/kg).

Replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	2994	3816	3588	3265	3279	3231	3539	2978	2890	3808	B_1 = 33389
2	3398	3814	3783	3717	3690	3617	3577	3833	2984	3030	B_2 = 35442
3	3592	3438	3381	3007	2907	2862	3788	3650	2962	3453	B_3 = 33040
Total	T_1=9983	T_2=11068	T_3=10752	T_4=9989	T_5=9876	T_6=9710	T_7=10905	T_8=10461	T_9=8836	T_9=10291	G= 101871
Mean	t'_1=3328	t'_2=3689	t'_3=3584	t'_4=3330	t'_5=3292	t'_6=3237	t'_7=3635	t'_8=3487	t'_9=2945	t'_9=3430	

Table 2 Data for total Ca concentration (mg/kg).

Replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	778	894	865	834	879	857	863	847	823	912	B_1 = 8554
2	849	889	891	884	879	882	867	892	844	841	B_2 = 8717
3	871	848	871	854	813	799	898	871	862	866	B_3 = 8553
Total	T_1=2498	T_2=2631	T_3=2628	T_4=2572	T_5=2571	T_6=2538	T_7=2628	T_8=2610	T_9=2529	T_9=2620	G= 25824
Mean	t'_1=833	t'_2=877	t'_3=876	t'_4=857	t'_5=857	t'_6=846	t'_7=876	t'_8=870	T'_9=843	t'_9=873	

Table 3 Data for total Co concentration (mg/kg).

Replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	1.54	1.56	1.33	1.67	1.57	1.52	1.68	1.46	1.38	1.60	B_1 = 15.32
2	1.37	1.47	1.79	1.54	1.58	1.63	1.44	1.80	1.74	1.22	B_2 = 15.58
3	1.52	1.45	1.58	1.67	1.51	1.93	1.36	1.58	1.48	1.61	B_3 = 15.68
Total	T_1=4.43	T_2=4.49	T_3=4.70	T_4=4.88	T_5=4.67	T_6=5.07	T_7=4.47	T_8=4.85	T_9=4.60	T_9=4.43	G= 46.58
Mean	t'_1=1.48	t'_2=1.50	t'_3=1.57	T'_4=1.63	t'_5=1.56	t'_6=1.69	t'_7=1.49	t'_8=1.62	t'_9=1.53	t'_9=1.48	

Table 4 Data for total Cr concentration (mg/kg).

Replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	6.24	5.50	4.60	5.94	6.34	6.53	5.46	6.54	5.60	5.78	B_1 = 58.53
2	5.60	4.87	5.87	6.20	5.28	6.12	5.51	5.95	7.40	5.38	B_2 = 58.19
3	5.31	5.65	5.19	5.82	5.95	5.84	6.70	5.92	6.41	5.55	B_3 = 58.35
Total	T_1=17.14	T_2=16.02	T_3=15.66	T_4=17.96	T_5=17.57	T_6=18.50	T_7=17.67	T_8=18.42	T_9=19.41	T_9=16.72	G= 175.08
Mean	t'_1=5.71	t'_2=5.34	t'_3=5.22	t'_4=5.99	t'_5=5.86	t'_6=6.17	t'_7=5.89	t'_8=6.14	t'_9=6.47	t'_9=5.57	

Table 5 Data for total Cu concentration (mg/kg).

Replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	5.90	6.79*	5.45	5.11	5.46	5.65	5.79	5.27	5.76	6.60	B_1 = 57.77
2	6.51	6.38	5.84	5.73	5.44	4.96	6.36	5.36	5.29	5.89	B_2 = 57.75
3	5.78	6.20	6.08	5.30	5.31	5.26	6.12	5.76	5.64	5.21	B_3 = 56.66
Total	T_1=18.19	T_2=19.37	T_3=17.37	T_4=16.14	T_5=16.20	T_6=15.88	T_7=18.26	T_8=16.39	T_9=16.69	T_9=17.70	G= 172.18
Mean	t'_1=6.06	t'_2=6.46	t'_3=5.79	t'_4=5.38	t'_5=5.40	t'_6=5.29	t'_7=6.09	t'_8=5.46	t'_9=5.56	t'_9=5.90	

*was identified as outlier

Table 6 Data for total Fe concentration (mg/kg).

Replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	846	907	842	875	874	894	864	878	844	892	B_1 = 8715
2	865	876	875	873	882	870	868	875	887	897	B_2 = 8769
3	866	853	879	871	884	869	889	865	895	881	B_3 = 8753
Total	T_1=2578	T_2=2636	T_3=2597	T_4=2619	T_5=2640	T_6=2633	T_7=2620	T_8=2618	T_9=2626	T_9=2670	G= 26237
Mean	t'_1=859	t'_2=879	t'_3=866	t'_4=873	t'_5=880	t'_6=878	t'_7=873	t'_8=873	t'_9=875	t'_9=890	

Table 7 Data for total Mg concentration (mg/kg).

Replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	613	774	744	647	667	668	721	604	583	781	B_1 = 6803
2	709	769	766	759	753	758	731	779	519	632	B_2 = 7175
3	739	697	711	597	620	575	769	738	609	691	B_3 = 6748
Total	T_1=2060	T_2=2240	T_3=2221	T_4=2003	T_5=2040	T_6=2002	T_7=2221	T_8=2121	T_9=1712	T_9=2105	G= 20726
Mean	t'_1=687	t'_2=747	t'_3=740	t'_4=668	t'_5=680	t'_6=667	t'_7=740	t'_8=707	t'_9=571	t'_9=702	

Table 8 Data for total Mn concentration (mg/kg).

Replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	6.14	6.36	6.04	6.41	6.24	6.33	6.09	6.61	6.36	6.23	B_1 = 62.82
2	6.31	5.96	6.35	6.01	6.23	6.02	6.18	6.33	6.61	6.58	B_2 = 62.56
3	6.26	6.02	6.46	6.45	6.49	6.43	6.73	5.95	6.63	6.22	B_3 = 63.64
Total	T_1=18.71	T_2=18.35	T_3=18.86	T_4=18.87	T_5=18.95	T_6=18.77	T_7=19.00	T_8=18.89	T_9=19.60	T_9=19.02	G= 189.02
Mean	t'_1=6.24	t'_2=6.12	t'_3=6.29	t'_4=6.29	t'_5=6.32	t'_6=6.26	t'_7=6.33	t'_8=6.30	t'_9=6.53	t'_9=6.34	

Table 9 Data for total P concentration (mg/kg).

Replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	273	290	263	288	280	286	286	258	247	300	B_1 = 2771
2	273	293	292	290	291	291	276	291	290	244	B_2 = 2832
3	282	283	265	267	288	284	293	282	262	277	B_3 = 2783
Total	T_1=827	T_2=867	T_3=820	T_4=846	T_5=860	T_6=860	T_7=855	T_8=831	T_9=798	T_9=821	G= 8386
Mean	t'_1=276	t'_2=289	t'_3=273	t'_4=282	t'_5=287	t'_6=287	t'_7=285	t'_8=277	t'_9=266	t'_9=274	

Table 11 Data for total S concentration (mg/kg).

Replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	857	859	768	829	892	791	858	880	802	833	B_1 = 8369
2	827	866	782	781	861	820	793	809	884	821	B_2 = 8245
3	838	791	787	828	822	748	807	756	923	817	B_3 = 8118
Total	T_1=2523	T_2=2517	T_3=2338	T_4=2438	T_5=2575	T_6=2358	T_7=2458	T_8=2445	T_9=2609	T_9=2472	G= 24732
Mean	T'_1=841	t'_2=839	t'_3=779	t'_4=813	t'_5=858	t'_6=786	t'_7=819	t'_8=815	t'_9=870	t'_9=824	

Table 12 Data for total Ti concentration (mg/kg).

Replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	381	431	345	409	378	392	412	332	313	405	B_1 = 3799
2	371	403	402	404	404	394	383	401	406	299	B_2 = 3866
3	386	391	354	349	391	390	412	398	319	385	B_3 = 3774
Total	T_1=1138	T_2=1225	T_3=1100	T_4=1163	T_5=1172	T_6=1176	T_7=1207	T_8=1131	T_9=1038	T_9=1089	G= 11438
Mean	t'_1=379	t'_2=408	t'_3=367	t'_4=388	t'_5=391	t'_6=392	t'_7=402	t'_8=377	t'_9=346	t'_9=363	

Table 13 Data for total V concentration (mg/kg).

Replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	10.6	11.1	9.8	10.9	10.3	10.4	10.9	9.7	10.0	11.3	B_1 = 105.0
2	10.6	10.1	10.3	11.2	10.6	10.3	10.4	10.6	11.0	9.5	B_2 = 104.6
3	10.4	10.3	10.1	10.2	10.2	10.5	10.9	11.1	9.9	10.6	B_3 = 104.3
Total	T_1=31.7	T_2=31.6	T_3=30.1	T_4=32.4	T_5=31.1	T_6=31.2	T_7=32.3	T_8=31.3	T_9=30.9	T_9=31.4	G= 313.9
Mean	t'_1=10.6	t'_2=10.5	t'_3=10.0	t'_4=10.8	t'_5=10.4	t'_6=10.4	t'_7=10.8	t'_8=10.4	t'_9=10.3	t'_9=10.5	

Table 14 Data for total Zn concentration (mg/kg).

Replicate	Sub-sample numbers										Total
	1	2	3	4	5	6	7	8	9	10	
1	27.6	30.3	28.0	29.6	28.8	29.4	28.3	29.1	28.7	29.9	**B_1 = 289.8**
2	28.5	28.6	29.2	28.9	28.6	29.1	28.0	29.1	30.2	30.3	**B_2 = 290.5**
3	28.3	28.1	31.2	28.9	30.5	28.6	30.2	28.1	30.9	29.0	**B_3 = 293.8**
Total	**T_1=84.4**	**T_2=87.1**	**T_3=88.4**	**T_4=87.4**	**T_5=87.9**	**T_6=87.2**	**T_7=86.5**	**T_8=86.3**	**T_9=89.8**	**T_9=89.3**	**G= 874.2**
Mean	**t'_1=28.1**	**t'_2=29.0**	**t'_3=29.5**	**t'_4=29.1**	**t'_5=29.3**	**t'_6=29.1**	**t'_7=28.8**	**t'_8=28.8**	**t'_9=29.9**	**t'_9=29.8**	

Appendix C

Homogeneity Testing of Candidate Ombrotrophic Peat Bog Reference Material

Homogeneity study for both total and acid-extractable concentration of Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, P, Pb, S, Ti, V, and Zn are carried out in the same way as for total Pb given in Chapter 4. Data for total and acid-extractable elemental concentration (mg/kg) (dry-weight (105°C) basis, i.e. corrected for moisture content of the air-dried peat) in the homogeneity testing of the candidate ombrotrophic peat (low ash) reference material are presented.

1. Homogeneity study of total Al concentration

Table 1a Data for total Al concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	3873	4025	3733	3877	21316	3
#2	3853	3921	3901	3891	1226	3
#3	3757	3732	3732	3740	215	3
#4	3717	3918	3716	3784	13564	3
#5	3686	3774	3829	3763	5215	3
#6	3661	3669	3705	3679	550	3
#7	3808	3849	3950	3869	5344	3
#8	3500	3856	3668	3675	31775	3
#9	3771	3741	3860	3790	3877	3
#10	3749	3868	3925	3847	8070	3
#11	3906	3430	3662	3666	56624	3
#12	3710	3920	3899	3843	13340	3
#13	3763	3976	3939	3893	12992	3
#14	3872	3882	3830	3861	747	3
#15	3944	3906	3841	3897	2679	3
#16	3804	4046	3919	3923	14536	3

Table 1b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*Df*	*MS*	F_{cal}	*P-value*	F_{critul}
Between Bottles	333579	15	22239	1.853	0.070	1.992
Within Bottles	384135	32	12004			
Total	717714	47				

From Table 1b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total Al concentration.

2. Homogeneity study of total Ca concentration

Table 2a Data for total Ca concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	859	923	885	889	1032	3
#2	897	907	899	901	29	3
#3	935	878	877	897	1074	3
#4	874	925	880	893	761	3
#5	851	890	895	879	578	3
#6	884	876	871	877	42	3
#7	891	909	895	898	92	3
#8	842	900	857	866	894	3
#9	848	858	889	865	458	3
#10	881	885	882	883	3	3
#11	876	812	848	845	1036	3
#12	883	879	859	874	162	3
#13	860	925	911	899	1183	3
#14	919	930	879	910	729	3
#15	914	900	894	903	102	3
#16	866	920	904	897	774	3

Table 2b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*Df*	*MS*	F_{cal}	*P-value*	$F_{critical}$
Between Bottles	13353	15	890	1.592	0.132	1.992
Within Bottles	17898	32	559			
Total	31252	47				

From Table 2b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total Ca concentration

3. Homogeneity study of total Co concentration

Table 3a Data for total Co concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	1.39	1.24	1.31	1.31	0.0055	3
#2	1.36	1.36	1.21	1.31	0.0079	3
#3	1.33	1.31	1.45	1.36	0.0054	3
#4	1.44	1.43	1.27	1.38	0.0096	3
#5	1.49	1.59	1.32	1.47	0.0195	3
#6	1.30	1.54	1.33	1.39	0.0172	3
#7	1.32	1.48	1.31	1.37	0.0096	3
#8	1.33	1.28	1.60	1.41	0.0299	3
#9	1.34	1.33	1.35	1.34	0.0001	3
#10	1.31	1.56	1.31	1.40	0.0211	3
#11	1.51	1.28	1.49	1.43	0.0169	3
#12	1.43	1.39	1.27	1.36	0.0065	3
#13	1.59	1.58	1.25	1.47	0.0372	3
#14	1.57	1.67	1.54	1.59	0.0050	3
#15	1.56	1.54	1.52	1.54	0.0003	3
#16	1.53	1.66	1.46	1.55	0.0100	3

Table 3b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	$F_{critical}$
Between Bottles	0.324	15	0.022	1.715	0.098	1.992
Within Bottles	0.403	32	0.013			
Total	0.728	47				

From Table 3b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total Co concentration.

4. Homogeneity study of total Cr concentration

Table 4a Data for total Cr concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	5.37	4.74	4.69	4.93	0.142	3
#2	4.73	4.82	4.81	4.79	0.002	3
#3	5.05	4.58	5.03	4.89	0.070	3
#4	5.01	5.16	4.88	5.01	0.020	3
#5	5.17	4.91	5.10	5.06	0.018	3
#6	4.95	5.13	4.63	4.90	0.063	3
#7	5.41	4.87	4.72	5.00	0.133	3
#8	4.93	4.98	5.09	5.00	0.007	3
#9	5.27	4.92	4.95	5.05	0.038	3
#10	5.01	5.06	5.00	5.02	0.001	3
#11	5.16	4.56	4.72	4.81	0.096	3
#12	4.74	4.71	4.64	4.70	0.003	3
#13	5.30	5.01	5.18	5.16	0.022	3
#14	4.82	5.37	4.92	5.03	0.086	3
#15	5.05	4.91	4.99	4.98	0.005	3
#16	4.86	4.71	5.08	4.88	0.035	3

Table 4b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*Df*	*MS*	F_{cal}	*P-value*	F_{critat}
Between Bottles	0.631	15	0.042	0.907	0.565	1.992
Within Bottles	1.484	32	0.046			
Total	2.115	47				

From Table 4b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total Cr concentration.

12. Homogeneity study of total Cu concentration

Table 5a: Data for total Cu concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	4.73	4.81	4.82	4.79	0.002	3
#2	4.06	4.93	4.13	4.37	0.233	3
#3	5.15	4.87	4.87	4.96	0.026	3
#4	4.85	5.19	4.92	4.99	0.032	3
#5	4.87	5.01	4.85	4.91	0.008	3
#6	5.06	4.97	5.02	5.02	0.002	3
#7	4.91	4.72	4.88	4.84	0.011	3
#8	4.06	5.29	4.93	4.76	0.404	3
#9	3.94	4.22	3.95	4.03	0.025	3
#10	3.75	4.18	3.98	3.97	0.046	3
#11	3.78	3.85	4.00	3.87	0.013	3
#12	3.92	4.16	4.15	4.08	0.019	3
#13	5.22	4.97	4.60	4.93	0.097	3
#14	5.16	5.28	5.03	5.16	0.016	3
#15	5.09	5.54	5.08	5.24	0.070	3
#16	5.08	5.48	5.20	5.25	0.042	3

Table 5b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	F_{crital}
Between Bottles	10.018	15	0.668	10.230	2.6798E-08	1.992
Within Bottles	2.089	32	0.065			
Total	12.107	47				

Although F_{cal} exceeds $F_{critical}$, the candidate peat bog reference material is considered inhomogeneous for total concentration of Cu. The submitted results from the inter-laboratory comparison showed no big spread of total Cu concentration.

6. Homogeneity study of total Fe concentration

Table 6a Data for total Fe concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	859	892	872	875	281	3
#2	890	873	873	879	89	3
#3	869	862	855	862	47	3
#4	852	873	886	870	303	3
#5	852	873	884	870	262	3
#6	877	876	858	870	112	3
#7	869	884	866	873	90	3
#8	881	887	849	872	415	3
#9	879	872	894	882	124	3
#10	912	898	897	902	72	3
#11	888	835	859	860	695	3
#12	903	883	864	883	380	3
#13	868	882	893	881	162	3
#14	886	909	898	898	139	3
#15	879	889	879	882	38	3
#16	878	870	887	878	73	3

Table 6b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	F_{critat}
Between Bottles	5569	15	371	1.811	0.078	1.992
Within Bottles	6560	32	205			
Total	12130	47				

From Table 6b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total Fe concentration.

7. Homogeneity study of total Mg concentration

Table 7a Data for total Mg concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	700	745	700	715	669	3
#2	708	717	706	710	33	3
#3	699	682	684	688	90	3
#4	682	720	677	693	565	3
#5	677	692	697	689	112	3
#6	669	666	674	670	17	3
#7	694	714	703	704	97	3
#8	681	793	755	743	3228	3
#9	694	685	720	700	339	3
#10	695	721	720	712	224	3
#11	719	643	685	682	1436	3
#12	692	716	710	706	161	3
#13	694	771	732	732	1512	3
#14	716	686	727	710	454	3
#15	754	718	733	735	335	3
#16	682	777	724	727	2247	3

Table 7b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	F_{critat}
Between Bottles	18554	15	1237	1.718	0.097	1.992
Within Bottles	23040	32	720			
Total	41594	47				

From Table 7b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total Mg concentration.

8. Homogeneity study of total Mn concentration

Table 8a Data for total Mn concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	6.22	6.27	6.32	6.27	0.002	3
#2	6.44	6.44	6.32	6.40	0.005	3
#3	6.24	6.20	5.89	6.11	0.036	3
#4	5.87	6.23	6.41	6.17	0.075	3
#5	6.35	6.24	6.97	6.52	0.156	3
#6	6.27	6.32	6.30	6.30	0.001	3
#7	6.24	6.27	6.09	6.20	0.009	3
#8	6.55	6.38	6.30	6.41	0.016	3
#9	6.16	6.33	6.18	6.22	0.009	3
#10	6.40	6.36	6.35	6.37	0.001	3
#11	6.21	5.90	6.52	6.21	0.095	3
#12	6.39	6.15	5.91	6.15	0.058	3
#13	5.76	6.00	6.17	5.98	0.042	3
#14	5.73	6.09	6.20	6.01	0.061	3
#15	6.08	6.08	6.96	6.37	0.259	3
#16	6.11	5.93	6.10	6.05	0.010	3

Table 8b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	$F_{critical}$
Between Bottles	1.093	15	0.073	1.396	0.208	1.992
Within Bottles	1.670	32	0.052			
Total	2.762	47				

From Table 8b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total Mn concentration.

9. Homogeneity study of total Na concentration

Table 9a Data for total Na concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	680	683	675	679	18	3
#2	696	686	683	688	51	3
#3	693	676	647	672	541	3
#4	645	669	685	666	412	3
#5	648	676	673	666	234	3
#6	670	679	663	671	62	3
#7	704	679	684	689	177	3
#8	675	695	679	683	110	3
#9	672	677	678	676	12	3
#10	684	691	693	689	22	3
#11	691	658	658	669	347	3
#12	688	682	673	681	54	3
#13	641	678	671	663	389	3
#14	644	668	651	655	156	3
#15	676	671	654	667	124	3
#16	664	656	669	663	41	3

Table 9b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	F_{critat}
Between Bottles	4977	15	332	1.929	0.058	1.992
Within Bottles	5504	32	172			
Total	10481	47				

From Table 9b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total Na concentration.

10. Homogeneity study of total P concentration

Table 10a Data for total P concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	282	292	270	281	123	3
#2	283	277	278	279	10	3
#3	277	269	288	278	93	3
#4	287	286	274	282	55	3
#5	275	279	274	276	7	3
#6	271	268	273	271	7	3
#7	271	285	276	277	47	3
#8	260	273	259	264	63	3
#9	280	261	281	274	124	3
#10	281	292	283	285	34	3
#11	279	256	263	266	131	3
#12	277	281	274	277	13	3
#13	277	299	283	286	133	3
#14	281	284	282	282	2	3
#15	279	274	293	282	103	3
#16	278	270	274	274	15	3

Table 10b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	F_{critat}
Between Bottles	1789	15	119	1.986	0.051	1.992
Within Bottles	1922	32	60			
Total	3711	47				

From Table 10b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total P concentration.

11. Homogeneity study of total Ti concentration

Table 11a Data for total Ti concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	428	410	373	404	801	3
#2	394	400	398	398	12	3
#3	376	381	385	381	24	3
#4	384	389	387	387	7	3
#5	404	404	401	403	3	3
#6	395	400	399	398	6	3
#7	403	408	401	404	13	3
#8	388	378	360	376	200	3
#9	411	377	397	395	298	3
#10	401	406	405	404	6	3
#11	411	377	370	386	485	3
#12	366	394	393	384	246	3
#13	395	410	401	402	57	3
#14	393	408	410	404	86	3
#15	391	383	403	393	101	3
#16	392	364	386	381	208	3

Table 11b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*Df*	*MS*	F_{cal}	*P-value*	F_{critat}
Between Bottles	4364	15	291	1.825	0.075	1.992
Within Bottles	5103	32	159			
Total	9467	47				

From Table 11b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total Ti concentration.

12. Homogeneity study of total V concentration

Table 12a Data for total V concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	9.98	9.62	10.04	9.88	0.052	3
#2	10.33	9.88	9.96	10.05	0.058	3
#3	10.18	9.81	9.09	9.69	0.307	3
#4	9.05	10.16	9.95	9.72	0.344	3
#5	9.82	9.68	9.99	9.83	0.025	3
#6	9.87	9.89	9.74	9.83	0.007	3
#7	9.65	10.05	9.69	9.80	0.049	3
#8	9.64	9.85	9.60	9.70	0.017	3
#9	10.11	10.04	10.07	10.07	0.001	3
#10	9.97	10.18	10.15	10.10	0.012	3
#11	10.20	9.88	9.60	9.90	0.088	3
#12	9.99	10.04	9.91	9.98	0.004	3
#13	9.74	9.93	9.47	9.71	0.053	3
#14	10.22	10.27	9.84	10.11	0.056	3
#15	9.80	9.44	10.05	9.76	0.096	3
#16	9.75	9.42	9.56	9.58	0.028	3

Table 12b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	$F_{critical}$
Between Bottles	1.227	15	0.082	1.092	0.401	1.992
Within Bottles	2.397	32	0.075			
Total	3.624	47				

From Table 12b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total V concentration.

13. Homogeneity study of total Zn concentration

Table 13a Data for total Zn concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	29.9	30.0	29.8	29.9	0.01	3
#2	29.5	30.4	29.8	29.9	0.22	3
#3	30.0	29.6	29.3	29.6	0.14	3
#4	29.2	29.5	29.6	29.4	0.05	3
#5	28.5	29.6	30.0	29.4	0.54	3
#6	29.5	30.0	29.5	29.6	0.08	3
#7	30.4	30.0	29.6	30.0	0.13	3
#8	29.9	30.2	29.5	29.9	0.14	3
#9	29.6	29.4	29.8	29.6	0.04	3
#10	30.5	29.9	29.8	30.1	0.12	3
#11	29.5	28.3	30.0	29.3	0.77	3
#12	30.0	29.3	28.7	29.3	0.43	3
#13	29.5	29.6	29.9	29.7	0.04	3
#14	29.2	30.5	29.9	29.9	0.44	3
#15	30.1	30.7	29.7	30.2	0.23	3
#16	29.8	30.7	30.2	30.2	0.24	3

Table 13b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	$F_{critical}$
Between Bottles	4.052	15	0.270	1.200	0.321	1.992
Within Bottles	7.202	32	0.225			
Total	11.253	47				

From Table 13b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total Zn concentration.

14. Homogeneity study of acid-extractable Al concentration

Table 14a Data for acid-extractable Al concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	2601	2300	2326	2409	27833	3
#2	2550	2593	2480	2541	3259	3
#3	2619	2511	2460	2530	6613	3
#4	2406	2462	2593	2487	9237	3
#5	2489	2336	2357	2394	6941	3
#6	2462	2565	2415	2481	5882	3
#7	2578	2516	2435	2509	5169	3
#8	2355	2399	2320	2358	1570	3
#9	2436	2320	2417	2391	3899	3
#10	2534	2601	2503	2546	2501	3
#11	2654	2498	2464	2539	10173	3
#12	2358	2422	2475	2418	3458	3
#13	2417	2312	2371	2367	2779	3
#14	2327	2480	2308	2372	8905	3
#15	2478	2498	2387	2454	3492	3
#16	2329	2357	2547	2411	13979	3

Table 14b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	F_{critat}
Between Bottles	209762	15	13984	1.934	0.058	1.992
Within Bottles	231382	32	7231			
Total	441144	47				

From Table 14b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for acid-extractable Al concentration.

15. Homogeneity study of acid-extractable Ca concentration

Table 15a Data for acid-extractable Ca concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	848	842	826	839	128	3
#2	843	834	833	837	30	3
#3	844	829	821	831	136	3
#4	837	833	844	838	32	3
#5	846	830	829	835	97	3
#6	827	834	816	826	85	3
#7	829	839	835	834	26	3
#8	816	825	796	812	217	3
#9	810	819	820	816	31	3
#10	811	818	815	815	13	3
#11	840	824	820	828	108	3
#12	812	820	816	816	18	3
#13	832	802	815	816	230	3
#14	798	831	837	822	439	3
#15	813	830	808	817	138	3
#16	806	805	847	819	578	3

Table 15b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	$F_{critical}$
Between Bottles	4030	15	269	1.864	0.068	1.992
Within Bottles	4612	32	144			
Total	8642	47				

From Table 15b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for acid-extractable Ca concentration.

16. Homogeneity study of acid-extractable Co concentration

Table 16a Data for acid-extractable Co concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	0.92	0.84	0.80	0.85	0.0040	3
#2	0.80	0.74	0.83	0.79	0.0025	3
#3	0.87	0.65	0.77	0.76	0.0121	3
#4	0.78	0.75	0.90	0.81	0.0062	3
#5	0.74	0.81	0.71	0.76	0.0026	3
#6	0.70	0.83	0.83	0.79	0.0059	3
#7	0.91	0.86	0.91	0.89	0.0009	3
#8	0.87	0.65	0.57	0.70	0.0250	3
#9	0.70	0.79	0.64	0.71	0.0057	3
#10	0.68	0.72	0.75	0.72	0.0014	3
#11	0.69	0.86	0.78	0.78	0.0077	3
#12	0.79	0.73	0.81	0.78	0.0018	3
#13	0.81	0.68	0.88	0.79	0.0099	3
#14	0.70	0.77	0.76	0.74	0.0014	3
#15	0.91	0.90	0.54	0.78	0.0447	3
#16	0.45	0.74	0.71	0.63	0.0256	3

Table 16b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	F_{critat}
Between Bottles	0.168	15	0.011	1.142	0.362	1.992
Within Bottles	0.315	32	0.010			
Total	0.483	47				

From Table 16b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for acid-extractable Co concentration.

17. Homogeneity study of acid-extractable Cr concentration

Table 17a Data for acid-extractable Cr concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	3.91	3.27	3.11	3.43	0.180	3
#2	3.49	3.55	3.16	3.40	0.043	3
#3	3.55	3.38	3.30	3.41	0.015	3
#4	3.11	3.01	3.41	3.18	0.045	3
#5	3.82	3.24	3.22	3.42	0.116	3
#6	3.23	3.63	3.30	3.39	0.046	3
#7	3.70	3.49	3.04	3.41	0.112	3
#8	2.93	3.00	3.13	3.02	0.010	3
#9	3.82	3.37	3.57	3.58	0.050	3
#10	3.45	3.70	3.33	3.49	0.035	3
#11	3.91	3.53	3.28	3.58	0.101	3
#12	3.16	3.38	3.49	3.34	0.028	3
#13	3.97	3.06	3.41	3.48	0.211	3
#14	3.31	3.64	3.39	3.45	0.030	3
#15	3.72	3.51	3.28	3.50	0.048	3
#16	3.00	3.19	3.64	3.27	0.108	3

Table 17b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	F_{critat}
Between Bottles	0.929	15	0.062	0.840	0.630	1.992
Within Bottles	2.360	32	0.074			
Total	3.289	47				

From Table 17b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for acid-extractable Cr concentration.

18. Homogeneity study of acid-extractable Cu concentration

Table 18a Data for acid-extractable Cu concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	3.47	3.93	3.96	3.78	0.075	3
#2	3.63	4.14	4.03	3.93	0.071	3
#3	3.12	3.92	3.74	3.59	0.177	3
#4	4.33	3.72	3.83	3.96	0.106	3
#5	3.52	3.63	3.66	3.60	0.005	3
#6	3.59	3.76	3.16	3.50	0.095	3
#7	3.35	3.22	4.18	3.58	0.275	3
#8	4.26	3.56	4.27	4.03	0.168	3
#9	3.55	3.37	3.12	3.35	0.046	3
#10	3.10	3.11	3.13	3.11	0.000	3
#11	3.53	3.15	3.06	3.25	0.062	3
#12	3.27	3.11	3.15	3.18	0.007	3
#13	3.94	2.73	3.17	3.28	0.372	3
#14	2.95	3.74	3.10	3.27	0.176	3
#15	3.54	3.50	3.12	3.39	0.055	3
#16	3.12	3.04	4.12	3.42	0.362	3

Table 18b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*Df*	*MS*	F_{cal}	*P-value*	F_{critat}
Between Bottles	3.741	15	0.249	1.944	0.056	1.992
Within Bottles	4.105	32	0.128			
Total	7.846	47				

From Table 18b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for acid-extractable Cu concentration.

19. Homogeneity study of acid-extractable Fe concentration

Table 19a Data for acid-extractable Fe concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	770	728	720	740	726	3
#2	749	746	735	743	56	3
#3	758	730	718	736	424	3
#4	728	722	754	735	292	3
#5	764	726	731	740	435	3
#6	733	746	718	732	193	3
#7	750	744	728	741	123	3
#8	714	727	695	712	263	3
#9	763	749	758	757	50	3
#10	751	773	753	759	143	3
#11	779	753	747	760	304	3
#12	724	731	737	731	41	3
#13	755	692	717	722	1010	3
#14	697	748	717	721	665	3
#15	730	734	702	722	308	3
#16	693	697	758	716	1340	3

Table 19b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	F_{crital}
Between Bottles	9721	15	648	1.627	0.121	1.992
Within Bottles	12746	32	398			
Total	22467	47				

From Table 19b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for acid-extractable Fe concentration.

20. Homogeneity study of acid-extractable Mg concentration

Table 20a Data for acid-extractable Mg concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	710	704	683	699	195	3
#2	704	704	696	701	24	3
#3	701	685	684	690	87	3
#4	689	690	707	695	101	3
#5	688	687	684	687	5	3
#6	685	691	671	682	102	3
#7	696	695	692	694	4	3
#8	679	677	644	667	384	3
#9	689	693	696	693	14	3
#10	697	703	698	699	8	3
#11	703	690	693	695	47	3
#12	670	681	683	678	48	3
#13	688	647	665	666	424	3
#14	650	676	668	664	178	3
#15	662	679	662	668	102	3
#16	655	655	694	668	503	3

Table 20b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	$F_{critical}$
Between Bottles	8414	15	561	4.033	0.000452	1.992
Within Bottles	4450	32	139			
Total	41594	47				

Although F_{cal} exceeds $F_{critical}$, the candidate peat bog reference material is considered inhomogeneous for acid-extractable concentration of Mg. The submitted results from the inter-laboratory comparison showed no big spread of acid-extractable Mg concentration.

21. Homogeneity study of acid-extractable Mn concentration

Table 21a Data for acid-extractable Mn concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	4.41	3.44	3.51	3.79	0.293	3
#2	3.56	3.69	3.33	3.52	0.034	3
#3	4.06	3.47	3.30	3.61	0.159	3
#4	3.33	3.25	3.66	3.41	0.046	3
#5	4.08	3.38	3.39	3.62	0.160	3
#6	3.38	3.55	3.23	3.39	0.027	3
#7	3.66	3.50	3.21	3.46	0.054	3
#8	3.21	3.24	3.25	3.23	0.000	3
#9	4.01	3.53	3.58	3.71	0.070	3
#10	3.41	3.82	3.35	3.53	0.066	3
#11	3.87	3.49	3.34	3.57	0.076	3
#12	3.30	3.25	3.53	3.36	0.023	3
#13	4.02	3.19	3.45	3.55	0.183	3
#14	3.29	3.64	3.26	3.40	0.046	3
#15	3.55	3.41	3.07	3.34	0.059	3
#16	3.03	3.13	3.77	3.31	0.161	3

Table 21b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	$F_{critical}$
Between Bottles	1.030	15	0.069	0.755	0.714	1.992
Within Bottles	2.913	32	0.091			
Total	3.943	47				

From Table 21b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for acid-extractable Mn concentration.

22. Homogeneity study of acid-extractable Na concentration

Table 22a Data for acid-extractable Na concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	187	215	181	194	327	3
#2	186	198	200	195	62	3
#3	203	198	162	188	504	3
#4	188	189	190	189	1	3
#5	203	186	198	196	80	3
#6	190	219	177	195	471	3
#7	198	173	217	196	483	3
#8	175	197	162	178	316	3
#9	196	200	197	198	5	3
#10	192	196	187	192	19	3
#11	197	202	200	200	5	3
#12	181	190	211	194	226	3
#13	199	214	188	200	166	3
#14	187	198	192	192	31	3
#15	176	195	177	183	111	3
#16	179	173	192	181	96	3

Table 22b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	F_{critat}
Between Bottles	1930	15	129	0.710	0.757	1.992
Within Bottles	5802	32	181			
Total	7732	47				

From Table 22b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for acid-extractable Na concentration.

23. Homogeneity study of acid-extractable P concentration

Table 23a Data for acid-extractable P concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	280	281	272	278	25	3
#2	281	278	280	280	4	3
#3	280	277	274	277	10	3
#4	281	283	287	284	11	3
#5	279	281	280	280	0	3
#6	281	274	279	278	14	3
#7	274	282	283	280	26	3
#8	275	279	265	273	48	3
#9	276	278	281	279	6	3
#10	281	282	284	282	3	3
#11	281	284	284	283	2	3
#12	275	280	276	277	8	3
#13	282	275	278	278	15	3
#14	275	283	284	281	25	3
#15	271	281	272	275	29	3
#16	277	276	288	280	43	3

Table 23b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	$F_{critical}$
Between Bottles	358	15	24	1.414	0.200	1.992
Within Bottles	540	32	17			
Total	897	47				

From Table 23b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for acid-extractable P concentration.

24. Homogeneity study of acid-extractable Pb concentration

Table 24a Data for acid-extractable Pb concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	152	155	156	154	5.2	3
#2	157	154	156	156	2.2	3
#3	155	155	155	155	0.2	3
#4	152	153	156	154	3.2	3
#5	154	150	160	155	23.4	3
#6	162	159	158	160	3.0	3
#7	152	165	155	157	44.9	3
#8	162	162	155	160	19.8	3
#9	151	157	155	154	8.6	3
#10	156	153	153	154	2.5	3
#11	154	156	155	155	1.5	3
#12	154	150	147	150	12.0	3
#13	157	151	153	154	10.0	3
#14	159	155	156	157	3.1	3
#15	157	162	154	158	17.5	3
#16	155	152	157	155	5.8	3

Table 24b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	$F_{critical}$
Between Bottles	262	15	17	1.719	0.097	1.992
Within Bottles	326	32	10			
Total	588	47				

From Table 24b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for acid-extractable Pb concentration.

25. Homogeneity study of acid-extractable Ti concentration

Table 25a Data for acid-extractable Ti concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	116	106	101	107	56	3
#2	99	107	100	102	22	3
#3	110	97	96	101	63	3
#4	92	96	107	98	62	3
#5	119	107	107	111	48	3
#6	105	102	99	102	8	3
#7	103	102	100	102	3	3
#8	94	98	96	96	3	3
#9	118	107	107	111	37	3
#10	106	112	102	107	24	3
#11	116	103	98	105	84	3
#12	95	103	105	101	29	3
#13	117	92	104	104	155	3
#14	96	106	94	99	45	3
#15	100	97	90	96	27	3
#16	91	93	100	95	22	3

Table 25b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	F_{critat}
Between Bottles	1144	15	76	1.775	0.085	1.992
Within Bottles	1374	32	43			
Total	2518	47				

From Table 25b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for acid-extractable Ti concentration.

26. Homogeneity study of acid-extractable V concentration

Table 26a Data for acid-extractable V concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	5.98	5.70	5.73	5.80	0.025	3
#2	6.45	6.29	5.82	6.19	0.109	3
#3	5.99	5.98	5.73	5.90	0.022	3
#4	5.65	5.96	5.88	5.83	0.025	3
#5	6.34	5.59	5.70	5.88	0.166	3
#6	5.54	6.02	5.48	5.68	0.089	3
#7	5.66	5.96	5.69	5.77	0.027	3
#8	5.95	5.95	5.52	5.81	0.061	3
#9	6.19	5.86	5.77	5.94	0.048	3
#10	5.87	5.86	5.55	5.76	0.033	3
#11	6.34	5.44	5.85	5.88	0.202	3
#12	5.37	5.50	5.74	5.54	0.036	3
#13	6.19	5.65	5.73	5.86	0.086	3
#14	5.61	6.37	5.47	5.81	0.234	3
#15	5.87	6.07	5.63	5.86	0.048	3
#16	5.39	5.26	5.99	5.55	0.151	3

Table 26b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	F_{critat}
Between Bottles	1.038	15	0.069	0.813	0.657	1.992
Within Bottles	2.725	32	0.085			
Total	3.764	47				

From Table 26b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for acid-extractable V concentration.

27. Homogeneity study of acid-extractable Zn concentration

Table 27a Data for acid-extractable Zn concentration.

Sample	Concentration (mg/kg)			Mean	Variance	n
	Replicate#1	Replicate#2	Replicate#3			
#1	29.1	28.0	27.1	28.0	0.997	3
#2	27.4	27.5	28.6	27.8	0.408	3
#3	32.0	28.3	26.6	29.0	7.739	3
#4	28.0	28.1	28.4	28.2	0.050	3
#5	27.8	26.8	27.2	27.3	0.264	3
#6	26.6	28.2	26.6	27.1	0.881	3
#7	27.0	27.7	27.2	27.3	0.135	3
#8	27.3	26.8	25.1	26.4	1.405	3
#9	27.1	27.0	27.4	27.2	0.044	3
#10	26.5	27.3	26.8	26.9	0.170	3
#11	27.0	27.5	27.2	27.2	0.067	3
#12	26.5	27.2	26.6	26.8	0.123	3
#13	28.5	26.1	27.0	27.2	1.443	3
#14	26.7	28.3	27.1	27.4	0.656	3
#15	26.6	27.6	26.5	26.9	0.356	3
#16	28.2	27.0	28.9	28.0	0.978	3

Table 27b Analysis of variance (ANOVA) for homogeneity testing.

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	F_{crital}
Between Bottles	18.590	15	1.239	1.262	0.281	1.992
Within Bottles	31.434	32	0.982			
Total	50.024	47				

From Table 27b, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for acid-extractable Zn concentration.

Appendix D

Inter-laboratory Comparison Material and Documents

1. Bottles of prepared candidate peat material NIMT/UOE/FM/001
2. Inter-laboratory comparison protocol
3. Pro forma A
4. Pro forma B

Figure 1 Bottles of prepared candidate peat material NIMT/UOE/FM/001.

Total and extractable contents of elements in ombrotrophic peat bog candidate reference material (low ash)

1. INTRODUCTION

This protocol describes the procedures to be followed by laboratories participating in the exercise to characterise an ombrotrophic peat bog candidate reference material (low ash) for (*i*) total and (*ii*) extractable contents of elements.

The total contents of elements can be determined by using non-destructive analytical techniques (XRF, INAA, etc.), or destructive analytical techniques employing ashing procedures, such as mixtures of mineral acids with HF for wet ashing or dissolution after dry ashing, alkaline fusion, etc, to decompose materials. The extractable contents of elements are conventionally defined by the procedures involving extraction with aqua-regia, extraction with boiling 2 M nitric acid, or extraction with cold 2 M nitric acid.

Participants are free to choose analytical methods of which they have previous experience and can therefore be expected to give valid results when applied by an experienced analyst. Alternatively, they can use analytical methods according to the protocol provided. Outlined below are some general aspects of working procedures that should be followed in the execution of a laboratory's chosen analytical methods. Participants are asked to make all reasonable effort to meet these requirements but, if this is not possible, the results will still be of value to the exercise, provided that information is given as to those aspects of the protocol that could not be followed.

2. WORKING PROCEDURES

2.1 Receipt of Samples

Check that samples (a unit of ombrotrophic peat bog candidate reference material and a unit of control material) have been received in an undamaged condition and that they are clearly labelled. If there is any problem with the samples, contact:

Dr. J.G. Farmer
Environmental Chemistry Unit
Department of Chemistry
Joseph Black Building
The King's Buildings
University of Edinburgh
West Mains Road
Edinburgh EH9 3JJ
Scotland, UK.
Telephone: +44 (0)131 6504757
Fax: +44 (0)131 6504757
E-mail address: J.G.Farmer@ed.ac.uk

2.2 Storage of Samples

Store the candidate reference material in the original unopened container at ambient temperature until the analyses are to be carried out.

2.3 Timescale

The analyses should be carried out, and the results reported to the study organiser within 8 to 10 weeks of receipt of the samples, if possible, to enable your results to be included in the data set for statistical evaluation.

2.4 Preparation of the Candidate Reference Material Sample

Allow the sample to equilibrate to ambient temperature. When you are ready to analyse the sample, mix and shake the entire contents of the unit by an appropriate means to ensure homogeneity. If necessary, transfer the mixed candidate reference material to an air-tight jar immediately after mixing. The analyses should now be carried out as soon as possible.

2.5 Preparation of Sub-samples for Analysis

When a sub-sample is taken for analysis, ensure that it is representative of the contents of the entire container. Ideally, the mass of the sub-sample taken for analysis should be measured using a balance that has been checked with certified weights that are traceable to a recognised certification body.

2.6 Number of Replicate Sub-samples to be Analysed

Five replicate sub-samples of the candidate reference material should be analysed. In addition, a result for the control material is also required. Participants should report the results of **ALL** the replicate analyses that they carry out and should **NOT** discard any result, unless they know a mistake has occurred during the analysis. Statistical evaluation of the data will be carried out by the study organiser.

2.7 Analytical Methods to be Used

Participants are free to use methods of their own choice. The selected methods should be ones with which the laboratories are familiar and which are expected to produce valid results for total and extractable contents of elements. Analytical methods which use solid samples (XRF, INAA) can also be employed for the determination of the total element contents. Please be sure to indicate the mass of material that was analysed. The candidate material has been proved to be homogeneous at 250 mg. For wet chemical analysis, participants can, if they wish, use the method according to the protocol provided [Adapted USEPA Method 3052 Protocol: Microwave-assisted HF/HNO_3 digestion of peat (total-total digestion method) and Adapted USEPA Method 3051 Protocol: Microwave-assisted HNO_3 digestion of peat (total-recoverable digestion method)].

2.8 Quantitative Determination of the Analytes

Where the analytes are determined by an instrumental technique, the response of the instrument should be calibrated using a reliable standard of the analyte in question. The calibration standard should be obtained from a recognised supplier and have appropriate documentation as to its concentration/purity and expiry date.

Before the sample is introduced to the instrument, it should be established that the instrumental response to replicate measurements of the standard is of acceptable repeatability, i.e. that the instrument response is stable with time. It should also be established that the instrument is being operated within its linear range.

The analyte concentration in the standard should be such that instrument responses for sample and standard are similar. Alternatively, a calibration graph may be constructed, in which case the sample

response should be similar to that observed for the mid-point of the graph. The results for the measurements should be examined to confirm that the instrument response has not altered significantly during the course of the measurements.

2.9 Analytes to be Characterised

2.9.1. Total element contents:

Participants are requested to carry out the analysis covering all or as many of the following elements as possible plus any others that individual participants would like to determine.

Aluminium, Iron, Sodium, Calcium, Lead, Arsenic, Mercury,
Nickel, Chromium, Magnesium, Manganese, Vanadium,
Titanium, Copper, Cadmium, Sulfur, Phosphorus, Zinc, etc.

2.9.2. Extractable content of elements:

Participants are requested to carry out the analysis covering all or as many of the following elements as possible plus any others that individual participants would like to determine.

Aluminium, Iron, Sodium, Calcium, Lead, Arsenic, Mercury,
Nickel, Chromium, Magnesium, Manganese, Vanadium,
Titanium, Copper, Cadmium, Sulfur, Phosphorus, Zinc, etc.

2.10 Reporting of Results

All results should be reported on the corresponding pro-forma provided, together with other relevant information. The results should be reported on the sample based on **'dry weight'** i.e. with correction for moisture content. Moisture content should be determined on non-analysed aliquots oven-dried at 105 °C until constant weight was obtained (ASTM D2974 -71 Standard Test Methods for Moisture, Ash, and Organic Matter of Peat Materials is also provided). Report results to two decimal places, in the units indicated on the pro-forma. The pro-forma should be returned to:

Dr. J.G. Farmer
Environmental Chemistry Unit
Department of Chemistry
Joseph Black Building
The King's Buildings
University of Edinburgh
West Mains Road
Edinburgh EH9 3JJ
Scotland, UK.
Telephone: +44 (0)131 6504757
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E-mail address: J.G.Farmer@ed.ac.uk

by 30/04/02 .

Ombrotrophic peat bog candidate reference material (low ash) characterised for total element contents

Please complete this form as fully as possible

1. LABORATORY IDENTIFICATION

Laboratory:.....

.....

Address:.....

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.....

.....

Telephone:.....

Fax:.....

E-mail:.....

Contact name:.....

2. TIMESCALES

Date samples received:.....

Date analysis started:.....

Storage conditions prior to analysis:.....

3. RESULTS

Analytes	Date of Analysis	Weight taken (g)	H_2O Content (%)	Units*	Result 1	Result 2	Result 3	Result 4	Result 5	Ctrl. Mat.
Al				mg/kg						
Ca				mg/kg						
Cd				mg/kg						
Co				mg/kg						
Cr				mg/kg						
Cu				mg/kg						
Fe				mg/kg						
Mg				mg/kg						
Mn				mg/kg						
Na				mg/kg						
Ni				mg/kg						
P				mg/kg						
Pb				mg/kg						
S				mg/kg						
Ti				mg/kg						
V				mg/kg						
Zn				mg/kg						
As				mg/kg						
Hg				mg/kg						

*Concentration values are based on dry weight

4. ANALYTICAL METHOD USED

☐ Microwave-assisted USEPA Method 3052

☐ Adapted USEPA Method 3052 Protocol: Microwave-assisted HF/HNO_3 digestion of peat (total-total digestion method)

☐ others (brief outline)

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5. COMMENTS AND SUPPLEMENTARY INFORMATION

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Please return the completed form, by 30/04/02 .

To: Dr. J.G. Farmer
Environmental Chemistry Unit
Department of Chemistry
Joseph Black Building
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Edinburgh EH9 3JJ
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E-mail address: J.G.Farmer@ed.ac.uk

Ombrotrophic peat bog candidate reference material (low ash) characterised for extractable content of elements

Please complete this form as fully as possible

1. LABORATORY IDENTIFICATION

Laboratory:.....

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2. TIMESCALES

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3. RESULTS

Analytes	Date of Analysis	Weight taken (g)	H_2O Content (%)	Units*	Result 1	Result 2	Result 3	Result 4	Result 5	Ctrl. Mat.
Al				mg/kg						
Ca				mg/kg						
Cd				mg/kg						
Co				mg/kg						
Cr				mg/kg						
Cu				mg/kg						
Fe				mg/kg						
Mg				mg/kg						
Mn				mg/kg						
Na				mg/kg						
Ni				mg/kg						
P				mg/kg						
Pb				mg/kg						
S				mg/kg						
Ti				mg/kg						
V				mg/kg						
Zn				mg/kg						
As				mg/kg						
Hg				mg/kg						

*Concentration values are based on dry weight

4. ANALYTICAL METHOD USED

☐ Microwave-assisted USEPA Method 3051

☐ Adapted USEPA Method 3051 Protocol: Microwave-assisted HNO_3 digestion of peat (total-recoverable digestion method)

☐ others (brief outline)

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5. COMMENTS AND SUPPLEMENTARY INFORMATION

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Appendix E

Characterisation and Certification of Candidate Ombrotrophic Peat Bog Reference Material

Raw data for the replicate results of total and acid-extractable elemental concentration submitted by participants (expressed as concentration of element, mg/kg, corrected for moisture content), along with the calculated mean, standard deviation and 95% confidence interval are shown.

Table 1 Raw data for the replicate results of total Cd concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	0.35 0.37 0.34 0.36 0.37 0.36 0.35 0.38 0.33 0.36 0.35 0.36 0.38 0.38 0.38 0.37 0.38 0.38	0.49 0.48 0.49 0.49 0.48	0.37 0.36 0.39 0.38 0.37	0.22 0.20	0.40 0.43 0.41 0.39 0.38	0.42 0.48 0.45 0.45 0.50 0.44	
Laboratory Mean	0.36	0.48	0.37	0.21	0.40	0.46	0.38
SD	0.01	0.00	0.01	0.01	0.02	0.03	0.10
95% CI	0.01	0.01	0.01	0.08	0.02	0.03	0.10

Table 2 Raw data for the replicate results of total Co concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab6	Mean of Laboratory Means
Concentration (mg/kg)	0.84 0.83 0.83 0.84 0.82 0.86 0.86 0.85 0.85 0.84 0.81 0.82 0.81 0.80	0.94 0.93 0.93 0.94 0.94	0.85 0.89 0.88 0.86 0.85	1.39 1.24 1.31 1.28 1.21	
Laboratory Mean	0.83	0.94	0.87	1.29	0.98
SD	0.02	0.00	0.02	0.07	0.21
95% CI	0.01	0.01	0.02	0.09	0.33

Table 3 Raw data for the replicate results of total Cr concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	5.90 5.70 5.64 5.70 5.47 6.20 6.01 6.03 5.96 5.85 6.01 6.49 5.93 6.27	6.09 6.57 6.76 6.93 6.98	6.11 5.94 6.54 5.90 6.08	3.20 3.61 3.94 4.10 2.56	6.17 5.81 6.22 6.13 6.24	7.27 6.45 7.00 6.96 8.04 6.27	
Laboratory Mean	5.94	6.66	6.11	3.48	6.11	7.00	5.89
SD	0.27	0.36	0.25	0.62	0.18	0.63	1.24
95% CI	0.05	0.45	0.32	0.77	0.22	0.66	1.30

Table 4 Raw data for the replicate results of total Cu concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab4	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	4.89 4.75 4.80 4.70 4.72 5.07 5.06 5.00 4.94 4.95 5.04 4.84 4.92 4.73 4.70	5.38 5.25 5.23 5.28 5.37	5.07 5.01 5.11 5.10 4.95	5.71 4.72 5.71 5.93 6.59	5.66 5.39 5.50 5.78 5.26	5.16 5.28 5.03 5.22 4.97	6.20 5.55 6.70 6.67	
Laboratory Mean	4.87	5.30	5.05	5.73	5.52	5.13	6.28	5.41
SD	0.14	0.07	0.07	0.67	0.21	0.13	0.54	0.48
95% CI	0.07	0.09	0.08	0.83	0.26	0.16	0.56	0.44

Table 5 Raw data for the replicate results of total Fe concentration.

Laboratory ID	Lab4	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	804 802 844 930 879	840 878 900 952 896	898 878 897 918 887	979 989 1034 1028 1218 1011	
Laboratory Mean	852	893	896	1043	921
SD	54	41	15	88	84
95% CI	67	50	19	93	134

Table 6 Raw data for the replicate results of total Mn concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	6.82 6.65 6.62 6.64 6.63 7.29 7.20 7.08 7.04 7.09 7.05 6.89 6.69 6.89	7.81 7.87 7.65 7.82 8.00	7.13 7.11 7.55 7.34 7.57	5.81 6.42 7.44 7.78 7.06	7.87 7.87 7.30 7.77 7.85	7.46 7.40 7.82 7.78 9.48 7.93	
Laboratory Mean	6.90	7.83	7.34	6.90	7.73	7.98	7.45
SD	0.23	0.12	0.22	0.79	0.24	0.76	0.47
95% CI	0.13	0.15	0.27	0.98	0.30	0.80	0.50

Table 7 Raw data for the replicate results of total Ni concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab4	Lab5	Lab6	Lab7	Mean of Lab Means
Concentration (mg/kg)	4.00 3.87 3.88 3.84 3.79 4.03 3.92 3.90 3.89 3.88	3.87 3.91 4.01 3.93 3.91	3.99 4.25 4.07 4.16 4.16	5.60 6.81 3.84 8.45 6.92	3.43 3.60 3.35 3.91 3.45	4.37 4.27 4.26 4.17 4.19	4.87 4.86 4.57 4.54 13.39 5.36	
Laboratory Mean	3.90	3.92	4.13	6.32	3.55	4.25	6.27	4.62
SD	0.07	0.05	0.10	1.72	0.22	0.08	3.50	1.33
95% CI	0.05	0.07	0.12	2.13	0.27	0.10	3.68	1.23

Table 8 Raw data for the replicate results of total V concentration.

Laboratory ID	Lab1	Lab2	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	7.22 7.18 7.09 7.17 7.01 7.67 7.60 7.50 7.41 7.37 7.65 7.52 7.47 7.50	7.48 7.36 7.42 7.48 7.49	6.12 7.50 6.52 6.40 5.95	9.98 9.62 10.04 9.42 9.56	8.05 7.89 8.19 8.15 9.29 8.05	
Laboratory Mean	7.38	7.45	6.50	9.72	8.27	7.86
SD	0.21	0.06	0.60	0.27	0.51	1.21
95% CI	0.12	0.07	0.75	0.34	0.54	1.51

Table 9 Raw data for the replicate results of total Zn concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab4	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	25.0 25.0 24.7 24.8 24.5 26.7 27.1 26.8 26.6 27.1 26.5 25.4 25.3 24.8 24.9 27.2 27.3 27.3 27.2	31.7 29.1 29.1 29.6 29.8	29.2 29.2 28.4 28.4 28.3	23.7 24.6 25.7 27.3 25.9	27.0 28.9 28.1 29.7 27.8	29.5 30.4 29.8 29.3 28.7	32.7 32.1 33.9 33.7 37.8 32.9	
Laboratory Mean	26.0	29.9	28.7	25.4	28.3	29.5	33.9	28.8
SD	1.1	1.1	0.5	1.4	1.0	0.6	2.0	2.8
95% CI	0.5	1.3	0.6	1.7	1.3	0.8	2.1	2.6

Table 10 Raw data for the replicate results of total As concentration.

Laboratory ID	Lab4	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	14.90 16.80 17.90 18.30 18.30	1.87 1.94 1.85 1.90 1.89	3.13 2.87 3.00 2.78 2.69 3.00 2.79 3.29 3.23 2.95 3.26 2.90	2.36 2.37 2.36 2.35 2.73 2.45	
Laboratory Mean	17.24	1.89	2.99	2.44	6.14
SD	1.44	0.03	0.20	0.15	7.41
95% CI	1.79	0.04	0.12	0.16	15.95

Table 11 Raw data for the replicate results of total Hg concentration.

Laboratory ID	Lab8	Lab9	Mean of Laboratory Means
Concentration (mg/kg)	0.164 0.171 0.178 0.160 0.168 0.162 0.157 0.161 0.158 0.158 0.164 0.164 0.166 0.175 0.166 0.159 0.175 0.168 0.162 0.159	0.176 0.178 0.174 0.171 0.171	
Laboratory Mean	0.165	0.174	0.169
SD	0.006	0.003	0.007
95% CI	0.003	0.004	0.059

Table 12 Raw data for the replicate results of total Al concentration.

Laboratory ID	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	2503 2490 3903 4189 3734	3767 3850 4279 4207 4172	3073 3177 3728 3708 5101 3151	
Laboratory Mean	3364	4055	3656	3692
SD	808	230	764	347
95% CI	1003	286	802	862

Table 13 Raw data for the replicate results of total Ca concentration.

Laboratory ID	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	347 400 821 863 821	914 900 894 885 882	340 463 423 530 634 630	
Laboratory Mean	650	895	503	683
SD	254	13	117	198
95% CI	315	16	123	492

Table 14 Raw data for the replicate results of total Mg concentration.

Laboratory ID	Lab5	Lab6	Mean of Laboratory Means
Concentration (mg/kg)	81 189 673 704 669	708 717 706 694 681	
Laboratory Mean	463	701	582
SD	302	14	168
95% CI	375	17	1512

Table 15 Raw data for the replicate results of total Na concentration.

Laboratory ID	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	602 618 609 642 613	645 669 685 648 670	1113 1183 1086 1220 1256 1162	
Laboratory Mean	617	663	1170	817
SD	15	17	64	307
95% CI	19	21	67	762

Table 16 Raw data for the replicate results of total P concentration.

Laboratory ID	Lab5	Lab6	Mean of Laboratory Means
Concentration (mg/kg)	248 267 255 270 259	279 256 263 279 278	
Laboratory Mean	260	271	265
SD	9	11	8
95% CI	11	13	71

Table 17 Raw data for the replicate results of total S concentration.

Laboratory ID	Lab5	Lab6	Mean of Laboratory Means
Concentration (mg/kg)	964 1014 919 1007 905	780 802 779 828 848	
Laboratory Mean	962	807	884
SD	50	30	109
95% CI	62	38	980

Table 18 Raw data for the replicate results of total Ti concentration.

Laboratory ID	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	349 336 338 367 321	368 384 376 366 390	339 334 348 346 403 339	
Laboratory Mean	342	377	352	357
SD	17	10	26	18
95% CI	21	13	27	44

Table 19 Raw data for the replicate results of acid-extractable Cd concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab4	Lab5	Lab6	Lab7	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	0.63 0.60 0.55 0.59	0.32 0.36 0.34 0.34	0.37 0.39 0.38 0.40 0.39	0.45 0.46 0.45 0.46 0.46	0.26 0.28 0.26 0.27 0.27	0.38 0.40 0.41 0.37 0.37	0.44 0.43 0.42 0.41 0.43	0.40 0.38 0.39 0.38 0.36 0.40	
Laboratory Mean	0.60	0.34	0.39	0.46	0.27	0.39	0.43	0.39	0.41
SD	0.03	0.02	0.01	0.01	0.01	0.02	0.01	0.02	0.09
95% CI	0.05	0.03	0.01	0.01	0.01	0.02	0.01	0.02	0.08

Table 20 Raw data for the replicate results of acid-extractable Co concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab6	Lab7	Lab9	Mean of Laboratory Means
Concentration (mg/kg)	0.97 0.95 0.93 0.93 0.94	0.59 0.63 0.68 0.69 0.70	0.53 0.52 0.50 0.54 0.85	0.74 0.73 0.75 0.81 0.83	0.59 0.54 0.53 0.53 0.51	0.78 0.69 0.81 0.79 0.81	
Laboratory Mean	0.94	0.66	0.59	0.77	0.54	0.78	0.71
SD	0.02	0.05	0.15	0.05	0.03	0.05	0.15
95% CI	0.02	0.06	0.18	0.06	0.04	0.06	0.15

Table 21 Raw data for the replicate results of acid-extractable Cr concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab4	Lab5	Lab6	Lab7	Lab9	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	5.63 5.61 5.63 5.27	2.89 3.01 2.65 2.91 3.00	1.62 1.53 1.66 1.60 1.65	4.34 4.38 4.24 4.07 4.11	2.32 2.52 2.62 2.65 2.62	3.84 3.98 4.00 3.53 3.55	4.54 4.98 5.48 5.18 5.18	4.59 5.23 3.98 3.82 3.94	5.25 5.03 4.49 5.30 4.68 5.30	
Laboratory Mean	5.53	2.89	1.61	4.23	2.55	3.78	5.07	4.31	5.01	3.89
SD	0.18	0.15	0.05	0.14	0.14	0.23	0.35	0.59	0.35	1.31
95% CI	0.28	0.18	0.06	0.17	0.17	0.28	0.43	0.73	0.37	1.00

Table 22 Raw data for the replicate results of acid-extractable Cu concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab4	Lab5	Lab6	Lab7	Lab8	Lab9	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	5.45 5.54 5.63 5.17	4.25 4.04 4.25 3.85	3.77 3.39 3.37 3.65 3.30	5.53 4.88 4.73 4.64 5.38	3.15 3.44 3.88 3.53 3.71	3.96 4.03 3.74 3.83 3.66	4.67 4.70 4.75 4.79 4.66	4.99 4.38 5.79 7.43 6.67	5.23 5.81 5.57 5.70 5.43	5.50 4.80 4.23 4.38 4.04 4.87	
Laboratory Mean	5.45	4.10	3.50	5.03	3.54	3.84	4.71	5.85	5.55	4.64	4.62
SD	0.20	0.19	0.20	0.40	0.28	0.15	0.06	1.23	0.23	0.53	0.85
95% CI	0.31	0.31	0.25	0.50	0.34	0.19	0.07	1.53	0.28	0.56	0.61

Table 23 Raw data for the replicate results of acid-extractable Fe concentration.

Laboratory ID	Lab2	Lab4	Lab5	Lab6	Lab7	Lab8	Lab9	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	471 496 618 630 662	931 947 905 903 894	811 869 877 834 896	810 798 766 779 805	738 759 753 770 713	589 573 598 578 587	846 870 888 872 895	901 819 775 876 814 904	
Laboratory Mean	575	916	857	792	747	585	874	848	774
SD	86	22	34	19	22	9	19	53	130
95% CI	107	27	42	23	27	12	23	56	109

Table 24 Raw data for the replicate results of acid-extractable Mn concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab4	Lab5	Lab6	Lab7	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	6.60 6.44 6.29 6.45	3.69 3.91 3.87 3.94 4.24	3.24 3.06 3.05 3.22 3.07	5.60 5.40 5.10 4.90 5.10	4.87 5.98 5.78 5.96 5.15	4.91 4.72 4.60 4.61 4.87	3.39 3.39 3.39 3.39 3.39	5.96 5.26 5.17 5.96 5.64 5.81	
Laboratory Mean	6.45	3.93	3.13	5.22	5.55	4.74	3.39	5.63	4.75
SD	0.13	0.20	0.09	0.28	0.51	0.14	0.00	0.35	1.17
95% CI	0.20	0.25	0.12	0.34	0.63	0.18	0.00	0.36	0.98

Table 25 Raw data for the replicate results of acid-extractable Ni concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab4	Lab5	Lab6	Lab7	Lab8	Lab9	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	5.29 4.34 4.60 4.85	2.98 3.26 3.36 3.11 3.39	2.54 2.49 2.45 2.59 2.49	3.85 3.88 3.77 3.37 3.64	3.43 3.27 3.32 3.35 3.13	3.35 4.13 3.65 3.72 3.76	2.96 2.99 2.89 2.96 2.97	6.01 4.51 5.26 4.26 7.59	4.27 4.53 4.17 4.20 4.26	4.08 4.00 3.50 3.88 3.56 4.10	
Laboratory Mean	4.77	3.22	2.51	3.70	3.30	3.72	2.95	5.53	4.29	3.85	3.78
SD	0.41	0.17	0.05	0.21	0.11	0.28	0.04	1.34	0.14	0.26	0.89
95% CI	0.65	0.21	0.07	0.26	0.14	0.35	0.05	1.67	0.18	0.28	0.64

Table 26 Raw data for the replicate results of acid-extractable Pb concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab4	Lab5	Lab6	Lab7	Lab8	Lab9	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	170 172 171 166	132 132 133 115 127	171 171 167 162 167	184 196 178 186 177	164 163 164 160 161	176 173 168 167 175	204 208 200 211 200	159 160 159 156 152	170 181 181 178 179	165 153 146 162 146 168	
Laboratory Mean	169	128	168	184	162	172	205	157	178	156	168
SD	2	8	4	8	2	4	5	3	5	10	20
95% CI	4	9	5	9	2	5	6	4	6	10	14

Table 27 Raw data for the replicate results of acid-extractable V concentration.

Laboratory ID	Lab1	Lab2	Lab5	Lab6	Lab9	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	7.25 7.34 7.24 7.06	5.09 5.46 5.19 5.39 5.43	6.51 9.68 8.74 10.21 7.44	6.02 5.96 5.95 5.86 5.86	6.95 7.05 7.11 7.06 6.96	6.73 6.19 5.83 6.73 6.06 6.68	
Laboratory Mean	7.22	5.31	8.51	5.93	7.03	6.37	6.73
SD	0.12	0.16	1.54	0.07	0.07	0.39	1.12
95% CI	0.18	0.20	1.91	0.09	0.09	0.41	1.18

Table 28 Raw data for the replicate results of acid-extractable Zn concentration.

Laboratory ID	Lab1	Lab2	Lab3	Lab4	Lab5	Lab6	Lab7	Lab8	Lab9	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	30.6 36.0 30.0 30.2	26.1 26.9 26.8 26.5	24.6 25.5 24.3 24.6 25.7	30.2 31.1 29.5 30.0 29.5	26.9 27.4 28.4 27.8 27.5	29.1 28.3 28.1 29.6 30.0	29.1 28.9 28.7 29.6 28.5	42.4 36.7 39.0 50.2 30.7	31.9 33.4 32.9 32.9 33.4	29.5 27.3 25.9 29.5 27.2 29.6	
Laboratory Mean	31.7	26.6	24.9	30.1	27.6	29.0	29.0	39.8	32.9	28.2	30.0
SD	2.9	0.4	0.6	0.7	0.5	0.8	0.4	7.2	0.6	1.6	4.2
95% CI	4.6	0.6	0.8	0.8	0.7	1.0	0.5	9.0	0.7	1.6	3.0

Table 29 Raw data for the replicate results of acid-extractable As concentration.

Laboratory ID	Lab2	Lab3	Lab4	Lab5	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	3.03 3.14 3.14 3.01	1.94 1.91 1.91 2.02 1.91	3.33 3.13 3.05 3.25 3.11	2.01 2.01 1.79 1.79 1.82	2.21 2.17 1.91 2.19 2.05 2.23	
Laboratory Mean	3.08	1.94	3.17	1.88	2.13	2.44
SD	0.07	0.05	0.11	0.12	0.12	0.63
95% CI	0.11	0.06	0.14	0.14	0.13	0.79

Table 30 Raw data for the replicate results of acid-extractable Hg concentration.

Laboratory ID	Lab4	Lab6	Mean of Laboratory Means
Concentration (mg/kg)	0.152 0.152 0.152 0.149 0.146	0.200 0.196 0.166 0.163 0.167	
Laboratory Mean	0.150	0.178	0.164
SD	0.003	0.018	0.020
95% CI	0.003	0.022	0.179

Table 31 Raw data for the replicate results of acid-extractable Al concentration.

Laboratory ID	Lab2	Lab5	Lab6	Lab7	Lab9	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	1600 1750 1800 1860 1960	2543 2797 2794 2858 2637	2817 2627 2765 2673 2682	1636 1605 1655 1650 1638	2733 2744 2865 2832 3019	3200 2981 3005 3546 3157 3174	
Laboratory Mean	1794	2726	2713	1637	2839	3177	2481
SD	134	131	77	19	115	203	618
95% CI	166	162	95	24	143	213	649

Table 32 Raw data for the replicate results of acid-extractable Ca concentration.

Laboratory ID	Lab5	Lab6	Lab9	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	822 829 830 831 821	829 833 830 834 839	865 895 894 869 905	529 495 469 531 488 539	
Laboratory Mean	827	833	886	509	763
SD	5	4	18	28	172
95% CI	6	5	22	30	274

Table 33 Raw data for the replicate results of acid-extractable Mg concentration.

Laboratory ID	Lab2	Lab5	Lab6	Lab9	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	550 640 600 610 600	704 718 725 722 711	717 712 730 729 706	740 755 764 754 769	922 867 817 938 850 934	
Laboratory Mean	600	716	719	757	888	736
SD	32	9	11	11	50	103
95% CI	40	11	13	14	53	128

Table 34 Raw data for the replicate results of acid-extractable Na concentration.

Laboratory ID	Lab5	Lab6	Lab10	Mean of Laboratory Means
Concentration (mg/kg)	191 199 182 188 155	181 199 187 176 179	265 253 339 440 353 259	
Laboratory Mean	183	184	318	229
SD	17	9	74	78
95% CI	21	11	77	193

Table 35 Raw data for the replicate results of acid-extractable P concentration.

Laboratory ID	Lab2	Lab5	Lab6	Lab7	Lab9	Mean of Laboratory Means
Concentration (mg/kg)	288 285 277 246 288	278 278 280 279 275	295 288 296 297 284	281 269 282 277 266	272 277 276 274 279	
Laboratory Mean	277	278	292	275	276	279
SD	18	2	6	7	2	7
95% CI	22	2	7	9	3	9

Table 36 Raw data for the replicate results of acid-extractable S concentration.

Laboratory ID	Lab2	Lab5	Lab6	Mean of Lab Means
Concentration (mg/kg)	4480 4570 4410 4440 4360	1045 1029 993 975 984	778 799 785 768 753	
Laboratory Mean	4452	1005	777	2078
SD	79	30	18	2059
95% CI	98	38	22	5116

Table 37 Raw data for the replicate results of acid-extractable Ti concentration.

Laboratory ID	Lab5	Lab6	Lab7	Mean of Laboratory Means
Concentration (mg/kg)	93 121 113 120 105	103 100 97 96 101	123 125 112 122 133 113	
Laboratory Mean	110	99	121	110
SD	12	3	8	11
95% CI	14	4	8	27

Raw data for the replicate results of total elemental concentration for following elements submitted by one or two laboratories (expressed as concentration of element, mg/kg, without correction for moisture content), along with the calculated mean and standard deviation are shown.

Ag

Laboratory ID.	Lab1
Concentration (mg/kg)	0.065
	0.065
	0.064
	0.067
	0.066
	0.062
	0.059
	0.058
	0.059
	0.059
Laboratory Mean	0.062
SD	0.003

Ba

Laboratory ID.	Lab1
Concentration (mg/kg)	23.80
	24.19
	23.97
	23.88
	23.99
	24.68
	24.54
	24.77
	24.97
	25.22
	26.32
	26.27
	26.14
	26.53
	26.53
Laboratory Mean	25.05
SD	1.04

Br

Laboratory ID.	Lab4
Concentration (mg/kg)	154.6 158.1 161.9 182.8 168.9
Laboratory Mean	165.3
SD	11.1

Ce

Laboratory ID.	Lab1
Concentration (mg/kg)	4.60 4.64 4.60 4.63 4.61 4.60 4.67 4.66 4.71 4.68
Laboratory Mean	4.64
SD	0.04

Dy

Laboratory ID.	Lab1
Concentration (mg/kg)	0.271 0.271 0.277 0.270 0.267 0.245 0.237 0.240 0.243 0.238
Laboratory Mean	0.256
SD	0.016

Er

Laboratory ID.	Lab1
Concentration (mg/kg)	0.157 0.154 0.158 0.155 0.151 0.139 0.135 0.139 0.136 0.131
Laboratory Mean	0.146
SD	0.010

Eu

Laboratory ID.	Lab1
Concentration (mg/kg)	0.084 0.086 0.085 0.085 0.085 0.080 0.081 0.082 0.083 0.080
Laboratory Mean	0.083
SD	0.002

Ga

Laboratory ID.	Lab4
Concentration (mg/kg)	2.80 1.70 2.70 2.20 2.40
Laboratory Mean	2.36
SD	0.44

Gd

Laboratory ID.	Lab1
Concentration (mg/kg)	0.301 0.304 0.305 0.304 0.303 0.268 0.271 0.274 0.271 0.269
Laboratory Mean	0.287
SD	0.017

Ho

Laboratory ID.	Lab1
Concentration (mg/kg)	0.054 0.054 0.054 0.053 0.053 0.047 0.047 0.047 0.047 0.046
Laboratory Mean	0.050
SD	0.004

La

Laboratory ID.	Lab1
Concentration (mg/kg)	2.24 2.21 2.16 2.16 2.15 2.25 2.30 2.31 2.31 2.34
Laboratory Mean	2.24
SD	0.07

Lu

Laboratory ID.	Lab1
Concentration (mg/kg)	0.0219 0.0217 0.0222 0.0217 0.0212 0.0191 0.0191 0.0198 0.0191 0.0186
Laboratory Mean	0.0204
SD	0.0014

Mo

Laboratory ID.	Lab1
Concentration (mg/kg)	0.458
	0.442
	0.433
	0.441
	0.431
	0.462
	0.440
	0.429
	0.431
	0.428
	0.451
	0.448
	0.449
	0.456
	0.461
	0.451
	0.442
	0.454
Laboratory Mean	0.445
SD	0.011

Nd

Laboratory ID.	Lab1
Concentration (mg/kg)	1.93
	1.94
	1.93
	1.96
	1.90
	1.83
	1.85
	1.84
	1.86
	1.85
Laboratory Mean	1.89
SD	0.05

Pr

Laboratory ID.	Lab1
Concentration (mg/kg)	0.520 0.526 0.520 0.523 0.520 0.506 0.512 0.513 0.520 0.513
Laboratory Mean	0.517
SD	0.006

Rb

Laboratory ID.	Lab1	Lab4	Mean of Laboratory Means
Concentration (mg/kg)	1.89 1.88 1.87 1.91 1.91 1.97 1.96 1.97 1.99 1.98 1.90 1.91 1.87 1.91 1.93 2.06 2.04 2.02 2.00 2.02	1.90 2.30 2.20 2.30 2.60	
Laboratory Mean	1.95	2.26	2.10
SD	0.06	0.25	0.22

Se

Laboratory ID.	Lab3*	Lab4	Mean of Laboratory Means
Concentration (mg/kg)	1.98 1.93 1.98 1.93 1.95	1.90 1.90 1.90 1.80 1.90	
Laboratory Mean	1.95	1.88	1.92
SD	0.03	0.04	0.05

*corrected for moisture content

Sm

Laboratory ID.	Lab1
Concentration (mg/kg)	0.347 0.346 0.357 0.356 0.345 0.321 0.326 0.327 0.328 0.327
Laboratory Mean	0.338
SD	0.014

Sr

Laboratory ID.	Lab1	Lab4	Mean of Laboratory Means
Concentration (mg/kg)	20.35	19.70	
	20.26	20.10	
	19.96	20.10	
	20.22	22.30	
	19.93	20.60	
	20.86		
	20.83		
	20.74		
	20.64		
	20.56		
	20.76		
	20.54		
	20.63		
	20.57		
	20.57		
	21.87		
	21.46		
	21.46		
	21.45		
	21.49		
Laboratory Mean	20.76	20.56	20.66
SD	0.54	1.02	0.14

Tb

Laboratory ID.	Lab1
Concentration (mg/kg)	0.046
	0.045
	0.046
	0.045
	0.044
	0.041
	0.041
	0.041
	0.040
	0.040
Laboratory Mean	0.043
SD	0.002

Th

Laboratory ID.	Lab1
Concentration (mg/kg)	0.561 0.558 0.566 0.564 0.573 0.520 0.508 0.510 0.506 0.523
Laboratory Mean	0.539
SD	0.028

Tl

Laboratory ID.	Lab1
Concentration (mg/kg)	0.059 0.061 0.059 0.059 0.059 0.062 0.060 0.057 0.056 0.056 0.057 0.057 0.057 0.056 0.056
Laboratory Mean	0.058
SD	0.002

Tm

Laboratory ID.	Lab1
Concentration (mg/kg)	0.023 0.022 0.023 0.022 0.022 0.021 0.020 0.020 0.020 0.019
Laboratory Mean	0.021
SD	0.001

U

Laboratory ID.	Lab1
Concentration (mg/kg)	0.240 0.247 0.252 0.247 0.243 0.248 0.244 0.250 0.247 0.241
Laboratory Mean	0.246
SD	0.004

Y

Laboratory ID.	Lab4
Concentration (mg/kg)	3.4 3.6 3.1 3.3 3.8
Laboratory Mean	3.4
SD	0.3

Yb

Laboratory ID.	Lab1
Concentration (mg/kg)	0.147 0.146 0.151 0.146 0.144 0.136 0.136 0.135 0.133 0.130
Laboratory Mean	0.140
SD	0.007

Zr

Laboratory ID.	Lab4
Concentration (mg/kg)	12.2 12.9 11.5 15.3 12.9
Laboratory Mean	13.0
SD	1.4

Raw data for the replicate results of acid-extractable elemental concentration for following elements submitted by one or two laboratories (expressed as concentration of element, mg/kg, corrected for moisture content), along with the calculated mean and standard deviation are shown.

Ba

Laboratory ID	Lab2
Concentration (mg/kg)	14.0 15.0 14.1 14.6 15.1
Laboratory Mean	14.6
SD	0.5

Cs

Laboratory ID	Lab2
Concentration (mg/kg)	0.068 0.074 0.058 0.060 0.066
Laboratory Mean	0.065
SD	0.006

In

Laboratory ID	Lab2
Concentration (mg/kg)	0.0232 0.0233 0.0229 0.0239 0.0235
Laboratory Mean	0.0234
SD	0.0004

La

Laboratory ID	Lab9
Concentration (mg/kg)	2.68 2.85 2.89 3.02 2.94
Laboratory Mean	2.88
SD	0.13

Mo

Laboratory ID	Lab2
Concentration (mg/kg)	0.36 0.39 0.38 0.33 0.35
Laboratory Mean	0.36
SD	0.02

Rb

Laboratory ID	Lab2
Concentration (mg/kg)	0.69 0.68 0.46 0.65 0.68
Laboratory Mean	0.63
SD	0.10

Sb

Laboratory ID	Lab3
Concentration (mg/kg)	0.52 0.51 0.51 0.50 0.57
Laboratory Mean	0.52
SD	0.03

Sr

Laboratory ID	Lab2
Concentration (mg/kg)	14.2 15.6 17.5 15.7 17.1
Laboratory Mean	16.0
SD	1.3

Tl

Laboratory ID	Lab2
Concentration (mg/kg)	0.0440 0.0463 0.0445 0.0453 0.0469
Laboratory Mean	0.0454
SD	0.0012

U

Laboratory ID	Lab2
Concentration (mg/kg)	0.157 0.186 0.145 0.154 0.159
Laboratory Mean	0.160
SD	0.015

Y

Laboratory ID	Lab2
Concentration (mg/kg)	0.73 0.77 0.76 0.80 0.84
Laboratory Mean	0.78
SD	0.04

Appendix F

Certificate of Measurement

NIMT

Certificate No. 001

National Institute of Metrology (Thailand)

75/7 Rama VI Road, Thungphayathai, Rajthevi, Bangkok 10400, Thailand

University of Edinburgh

School of GeoSciences, Joseph Black Building, The King's Buildings,

West Mains Road, Edinburgh EH9 3JJ, UK

CERTIFICATE OF MEASUREMENT

Certified Reference Material: NIMT/UOE/FM/001

Total and acid-extractable elemental concentrations in ombrotrophic peat bog (low ash) reference material

Date of Issue:....01/05/04.....

Signed:.....

Dr. J. G. Farmer

University of Edinburgh

CERTIFIED VALUES_1

Certified values with uncertainties (coverage factor of 2) and information-only (italics) values [± 1 SD (n ≤ 4)] for the total elemental concentration of the ombrotrophic peat (low ash) reference material NIMT/UOE/FM/001.

Element	No. of Laboratories	Concentration[1] (mg/kg)
Al	*3*	*3692 ± 347*
As	*3*	*2.44 ± 0.55*
Ca	*3*	*683 ± 198*
Cd	6	0.38 ± 0.08
Co	3	0.88 ± 0.09
Cr	5	6.36 ± 0.44
Cu	6	5.28 ± 1.04
Fe	*4*	*921 ± 84*
Hg	*2*	*0.169 ± 0.007*
Mg	*2*	*582 ± 168*
Mn	5	7.52 ± 0.41
Na	*3*	*817 ± 307*
Ni	6	4.10 ± 0.37
P	*2*	*265 ± 8*
Pb	6	174 ± 8
Ti	*3*	*357 ± 18*
V	5	7.82 ± 1.08
Zn	7	28.6 ± 1.9

Note:
1. Concentration based on dry weight (105°C)

CERTIFIED VALUES_2

Certified values with uncertainties (coverage factor of 2) and information-only (italics) values [± 1 SD (n ≤ 4)] for the acid-extractable elemental concentration of the ombrotrophic peat (low ash) reference material NIMT/UOE/FM/001.

Element	No. of Laboratories	Concentration[1] (mg/kg)
Al	6	2481 ± 514
As	5	2.44 ± 0.58
Ca	*4*	*763 ± 172*
Cd	7	0.36 ± 0.05
Co	6	0.71 ± 0.13
Cr	9	3.90 ± 0.90
Cu	9	4.48 ± 0.73
Fe	6	839 ± 54
Hg	*2*	*0.164 ± 0.020*
Mg	5	737 ± 95
Mn	8	4.74 ± 0.87
Na	*3*	*229 ± 78*
Ni	8	3.44 ± 0.40
P	5	281 ± 7
Pb	8	169 ± 8
Ti	*3*	*110 ± 11*
V	5	6.37 ± 0.73
Zn	9	28.7 ± 1.6

Note:
1. Concentration based on dry weight (105°C)

MATERIAL PREPARATION

Peat was collected from the ombrotrophic peat bog at Flanders Moss, Scotland, in 2001. The material was air-dried to a moisture content of 10%, milled, sieved, and mixed in a glass jar on a roller bed for homogenisation.

PACKING

Supplied are 30 g of powdered ombrotrophic peat, with a particle size less than 2 mm in a screw-cap bottle.

HOMOGENEITY ASSESSMENT

The material was tested for homogeneity by determining elements of interest in randomly selected samples prepared for analysis according to the total and acid-extractable digestion methods using ICP-OES. The material was judged to be homogeneous as the variation between the samples tested was not significantly greater than the method variation.

STABILITY ASSESSMENT

The material has been tested for stability by analysing selected samples which have been stored at various temperatures (-20°C, 4°C, 20°C, 40°C) over a period of time using ICP-OES. No instability was observed at a temperature below 20°C.

CERTIFICATION

This material has been certified by co-operation between the School of GeoSciences, University of Edinburgh, a further 13 participant laboratories and the National Institute of Metrology (Thailand), by means of an inter-laboratory comparison exercise. This involved the analysis of samples of the material by participants using methods for the determination of the total and acid-extractable concentrations of elements in soil samples. The certified values are based on the means of laboratory means following elimination of outlying results. They relate to a minimum sample weight of 250 mg for determination of the total and acid-extractable element concentrations. The uncertainty was calculated according to a modification of the Guide on the Expression of Uncertainty in Measurement (GUM). Where concentration data were not sufficient and considered too variable, the arithmetic means are given as information-only (± 1 S.D.) values for some elements.

In addition to elemental concentration data, information on Pb isotopic composition was provided by three laboratories. Reported mean values of 1.1766 ± 0.0008, 1.1759 ± 0.0006, and 1.1765 ± 0.0003, yielded an overall information value of 1.176 ± 0.0004 (± 1 S.D.) for the $^{206}Pb/^{207}Pb$ ratio.

ANALYTICAL METHODS USED

For determination of the total elemental concentrations by destructive analytical techniques, ashing procedures capable of total decomposition of the materials should be used, such as mixtures of mineral acids with HF for wet ashing or ash dissolution after dry ashing, alkaline fusion, and microwave-assisted USEPA Method 3052[1], etc. The acid-extractable concentrations of elements are conventionally defined by the procedures involving extraction with HNO_3, aqua-regia, boiling 2 M HNO_3, or cold 2 M HNO_3.

INSTRUCTIONS FOR USE

The material should be kept in its original bottle and stored at temperatures between 4°C and 20°C. It should not be exposed to intensive sources of radiation or sunlight. Before opening, the contents should be brought to ambient temperature and then thoroughly mixed by repeated inversion of the bottle. The moisture content of the material should be determined on a separate aliquot oven-dried to constant weight at 105°C and analytical results then expressed on a dry weight basis.

SHELF LIFE

Provided the sample is stored under the appropriate conditions, its certification will remain valid for 24 months from date of shipment.

REFERENCES

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PARTICIPANTS

The number of participants' results used in the calculation of the certified values is given in the table of certified values on page 2 and page 3. The following participants took part in the inter-laboratory comparison exercise:

1. School of GeoSciences, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK.
2. Macaulay Institute, Craigiebuckler, Aberdeen AB15 8QH, UK
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13. Department of Chemistry, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway
14. Department of Earth Science and Engineering, Imperial College London, London SW7 2BP, UK; Department of Mineralogy, The Natural History Museum, London SW7 5AZ, UK.

LEGAL NOTICE

Appendix G

Isotopic Ratios in the Flanders Moss Peat Core Collected in 1999

Table 1 $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$, and $^{208}Pb/^{207}Pb$ ratios in the Flanders Moss peat core collected in 1999.

Sample depth (cm)	$^{206}Pb/^{207}Pb \pm 1SD.$	$^{208}Pb/^{206}Pb \pm 1SD.$	$^{208}Pb/^{207}Pb \pm 1SD.$
0-2	1.141 ± 0.0030	2.412 ± 0.0045	2.113 ± 0.0031
2-3	1.130 ± 0.0048	2.396 ± 0.0037	2.146 ± 0.0071
3-4	1.125 ± 0.0045	2.389 ± 0.0100	2.149 ± 0.0054
4-5	1.124 ± 0.0040	2.385 ± 0.0048	2.162 ± 0.0060
5-6	1.124 ± 0.0045	2.391 ± 0.0019	2.145 ± 0.0020
6-7	1.121 ± 0.0013	2.396 ± 0.0027	2.136 ± 0.0037
7-8	1.127 ± 0.0016	2.403 ± 0.0021	2.131 ± 0.0031
8-9	1.122 ± 0.0040	2.405 ± 0.0049	2.144 ± 0.0049
9-10	1.122 ± 0.0011	2.400 ± 0.0032	2.140 ± 0.0034
10-11	1.127 ± 0.0024	2.407 ± 0.0049	2.135 ± 0.0029
11-12	1.125 ± 0.0011	2.404 ± 0.0027	2.138 ± 0.0017
12-13	1.130 ± 0.0064	2.395 ± 0.0037	2.141 ± 0.0039
13-14	1.134 ± 0.0022	2.410 ± 0.0043	2.126 ± 0.0060
14-15	1.128 ± 0.0068	2.429 ± 0.0029	2.121 ± 0.0033
15-16	1.130 ± 0.0032	2.424 ± 0.0039	2.118 ± 0.0017
16-17	1.132 ± 0.0020	2.417 ± 0.0050	2.135 ± 0.0032
17-18	1.134 ± 0.0011	2.418 ± 0.0036	2.132 ± 0.0040
18-19	1.134 ± 0.0014	2.417 ± 0.0020	2.131 ± 0.0013
19-20	1.136 ± 0.0007	2.419 ± 0.0014	2.129 ± 0.0018
20-21	1.134 ± 0.0010	2.414 ± 0.0018	2.130 ± 0.0012
21-22	1.133 ± 0.0026	2.420 ± 0.0078	2.135 ± 0.0033
22-23	1.133 ± 0.0014	2.414 ± 0.0014	2.130 ± 0.0014
23-24	1.142 ± 0.0008	2.425 ± 0.0033	2.124 ± 0.0031
24-25	1.157 ± 0.0013	2.434 ± 0.0026	2.103 ± 0.0031
25-26	1.159 ± 0.0011	2.439 ± 0.0036	2.104 ± 0.0027
26-27	1.166 ± 0.0013	2.449 ± 0.0046	2.100 ± 0.0037
27-28	1.169 ± 0.0015	2.452 ± 0.0053	2.097 ± 0.0043
28-29	1.173 ± 0.0016	2.453 ± 0.0042	2.091 ± 0.0032
29-30	1.169 ± 0.0008	2.453 ± 0.0006	2.097 ± 0.0015
30-31	1.172 ± 0.0015	2.458 ± 0.0038	2.098 ± 0.0043
31-32	1.174 ± 0.0020	2.460 ± 0.0051	2.094 ± 0.0051
32-33	1.176 ± 0.0019	2.458 ± 0.0038	2.090 ± 0.0039
33-34	1.176 ± 0.0042	2.459 ± 0.0083	2.092 ± 0.0046
34-35	1.175 ± 0.0031	2.460 ± 0.0055	2.094 ± 0.0024
35-36	1.172 ± 0.0048	2.454 ± 0.0073	2.093 ± 0.0048
36-37	1.164 ± 0.0042	2.450 ± 0.0066	2.105 ± 0.0110
37-38	1.157 ± 0.0045	2.443 ± 0.0086	2.111 ± 0.0071
38-39	1.172 ± 0.0042	2.454 ± 0.0053	2.095 ± 0.0058
39-40	1.172 ± 0.0021	2.449 ± 0.0056	2.089 ± 0.0078
40-41	1.169 ± 0.0018	2.455 ± 0.0034	2.100 ± 0.0051
41-42	1.173 ± 0.0030	2.455 ± 0.0024	2.092 ± 0.0057
42-43	1.160 ± 0.0023	2.436 ± 0.0038	2.100 ± 0.0051

PAPER

Development of an ombrotrophic peat bog (low ash) reference material for the determination of elemental concentrations†

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Given the increasing interest in using peat bogs as archives of atmospheric metal deposition, the lack of validated sample preparation methods and suitable certified reference materials has hindered not only the quality assurance of the generated analytical data but also the interpretation and comparison of peat core metal profiles from different laboratories in the international community. Reference materials play an important role in the evaluation of the accuracy of analytical results and are essential parts of good laboratory practice. An ombrotrophic peat bog reference material has been developed by 14 laboratories from nine countries in an inter-laboratory comparison between February and October 2002. The material has been characterised for both acid-extractable and total concentrations of a range of elements, including Al, As, Ca, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, P, Pb, Ti, V and Zn. The steps involved in the production of the reference material (*i.e.* collection and preparation, homogeneity and stability studies, and certification) are described in detail.

Introduction

Environmental samples such as tree rings, mosses, aquatic sediments, snow, ice, and peat have been used as archives for the study of atmospheric metal deposition.[1–3] The surface layers in ombrotrophic raised bogs are isolated from the influence of local ground water and surface water, and receive their inorganic content by atmospheric deposition only.[4] Ombrotrophic peat that has accumulated during the past hundreds or thousands of years, therefore, can be used to study vegetation history, climate change, and, in principle, the historical trend of atmospheric metal deposition. Most recent

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relevant research results,[5–9] *e.g.* for Pb, have been consistent with information from other archives, including lake sediments and ice cores, and are compatible with known historical trends where available, *e.g.* the emission of Pb from different sources. Given the increase in this type of study, the lack of a common, validated sample preparation method and of a certified peat reference material has hindered not only the quality assurance of the generated analytical data but also the interpretation and comparison of peat core metal profiles from different laboratories in the international community. Instead of using an authentic peat reference material, quality control in this sort of study has long been referred to certified reference materials (CRMs) developed for plants and soils. Although an attempt, as yet uncompleted, was made to develop a peat reference material for quality control use by laboratories in the international peat bog community,[10] the material was of fen origin and had high ash content (~20%), uncharacteristic of ombrotrophic peat bogs. In addition, different laboratories in this field of research currently adopt a wide range of practices, including the determination of acid-extractable and of total elemental concentrations by various instrumental analytical techniques. To compare and standardise these different approaches, we developed a new candidate peat reference material, derived from an ombrotrophic bog, and subjected it to an international inter-laboratory study as part of the certification process.

The total concentrations of elements can be determined by using non-destructive analytical techniques (XRF, INAA, *etc.*) or destructive analytical techniques employing ashing procedures, such as mixtures of mineral acids with HF for wet ashing or dissolution after dry ashing, alkaline fusion *etc.*, followed by AAS, ICP-OES, ICP-MS *etc.* The acid-extractable concentrations of elements are conventionally defined by the procedures involving extraction with aqua regia, boiling 2 M HNO_3, or cold 2 M HNO_3.[11] Reference materials characterised for both acid-extractable and total concentrations of elements are of value to laboratories that cannot or do not employ HF to achieve total dissolution of aluminosilicate minerals in sample matrices.

Methods

Collection and preparation of the candidate ombrotrophic peat reference material

On 11 September, 2001, the starting material was collected from the ombrotrophic peat bog at Flanders Moss, near Stirling, Scotland. Vegetation on top of the bog was removed using a stainless steel knife and the peat sample dug up by a spade from a depth of ~30 cm in blocks of approximate size 20 cm × 20 cm × 30 cm. Seven blocks of peat of about the same size were collected, yielding a total wet weight of ~70 kg. The wet peat was wrapped up in a polyethylene bag and transported to the Macaulay Institute, Aberdeen, UK, the following day. It was then divided into sub-samples, from which root material was extracted by hand, and air-dried at 30 °C for 10 days on paper-lined aluminium trays. The dried peat was then broken into small aggregates with a wooden hammer and air-dried for a further week. Ten sub-samples were then randomly taken from the drying trays. The moisture content based on oven-drying at 105 °C was determined on each sub-sample, yielding a mean moisture content of ~10% in 30 °C air-dried peat. The air-dried peat was milled to less than 2 mm in particle size with a stainless steel hammer mill (Christie Hunt). Approximately 4.5 kg of peat material was obtained and transferred into a 20-litre glass jar, which was placed on a roller bed for two weeks.

Preliminary study of homogeneity

Ten sub-samples (~2 g each) were randomly taken from the jar and analysed for metal concentrations to make a preliminary assessment of the bulk homogeneity using a modified version of ASTM 826-85 "Standard practice for testing homogeneity of material for development of reference material".[12] This mainly involved the selection of test sub-samples from the bulk material, digestion and analysis of sub-samples (0.25 g), and statistical treatment of the measurement data using the ASTM 826-85 standard protocol. The total concentration for each element of interest was the variable we evaluated to assess homogeneity. The USEPA Method 3052 Protocol[13] was modified for the digestion of sub-samples, carried out by microwave-assisted HF–HNO_3 digestion of peat (total-total digestion method). This method consisted of a representative sample of up to 0.25 g (the initial weight) being ashed at 450 °C for 4 h prior to digestion in 9 ml of concentrated HNO_3 and 0.5 ml HF for about 15 minutes using microwave heating with a suitable laboratory microwave system. The sample and acid are placed in suitably inert polymeric microwave vessels. The vessel is sealed and heated in the microwave system. The temperature profile is specified to permit specific reactions and incorporates reaching 180 ± 5 °C in ~5.5 minutes and remaining at 180 ± 5 °C for 9.5 minutes for the completion of specific reactions. After cooling, the vessel contents are filtered, evaporated to ~1 ml, and then diluted to volume and analysed by FAAS, GFAAS, ICP-OES, or ICP-MS.

Following the preliminary homogeneity tests, the peat material was further homogenised by mixing in the jar on the roller bed for another week. The roller bed was then stopped, and peat material was taken from the jar to fill a series of five pre-cleaned amber glass bottles, each containing a minimum of 30 g. After that, they were promptly closed using polyethylene screwcaps. The glass jar was again rotated for another five minutes and the next five bottles were filled in the same way. The cycle was repeated until a total of 145 (29 × 5) bottles of candidate peat reference material were finally obtained. About ten percent of the bulk peat material that was left on the bottom of the jar was discarded, just in case it was less homogeneous.[14,15] Twenty-nine bottles (one from each series) were set aside for homogeneity and stability testing. The candidate ombrotrophic peat bog reference material was then named NIMT/UOE/FM/001. The ash content (450 °C) of this material was ~4–5% of the 30 °C air-dried weight.

Homogeneity testing

Homogeneity testing for total and acid-extractable concentrations of elements in the candidate ombrotrophic peat bog reference material was carried out by using the *F*-test and ANOVA statistical test. Sixteen (three times the cube root of *n* units)[16] bottles of candidate peat bog reference material were randomly selected from the 29 bottles that had been set aside earlier. As before, microwave-assisted HF–HNO_3 digestion of peat (total–total digestion method), a modification of the USEPA Method 3052 Protocol, was utilised for total element concentration, while microwave-assisted HNO_3 digestion of peat (total–extractable digestion method), a modification of the USEPA Method 3051 Protocol,[17] yielded acid-extractable element concentration. The latter digestion method employs 10 ml of HNO_3 as reagent instead of the HNO_3–HF mixture used in the former.

Stability study

The stability of the candidate peat bog reference material was tested by storing bottles of the candidate reference material at −20 °C, +4 °C, +20 °C, and +40 °C for a period of 12 months. After 1, 3, 6 and 12 months, the total and acid-extractable elemental concentrations were determined (in five replicates). The procedures were the same as those used in the homogeneity study. Instability would be detected by comparing the

measured element concentrations of samples stored at +4 °C, +20 °C, +40 °C with those of samples stored at −20 °C as determined at various times over 12 months. The samples stored at −20 °C were used as reference for the samples stored at +4 °C, +20 °C and +40 °C, respectively.

Certification of concentration

An international inter-laboratory comparison exercise was conducted to certify the reference material. Laboratories invited to take part in the certification exercise were those of experienced research groups in this field of study, considered to be well-equipped and employing quality control and quality assurance procedures. The 14 laboratories taking part were requested to verify the quality of their measurements, in particular, the validity of calibration (including calibration of balances, volumetric glasswares and other tools of relevance). Participants were free to choose analytical methods of which they had previous experience and could therefore be expected to give valid results when applied by an experienced analyst. They were also asked to make a minimum of five independent replicate determinations of each element in the candidate reference material, each laboratory being supplied with one bottle of prepared peat material.

On receipt of data from participants, an identification number (Laboratory ID) was assigned to each laboratory. Where there were two separate sets of data, *i.e.* one for total elemental concentration and another for acid-extractable element concentration, the Laboratory ID for the latter set is not necessarily the same as that for the former set. Nine laboratories reported data for total (HNO_3–HF, HNO_3–HBF_4, HNO_3–H_2O_2–H_2O–HF) concentrations, and ten laboratories for acid-extractable (HNO_3, HNO_3–HCl, HNO_3–$HClO_4$) concentrations, using a range of digestion conditions and a variety of analytical techniques (AAS, GFAAS, ICP-OES, ICP-MS), including, in the case of one laboratory, XRF analysis of the solid phase, and, in two others, thermal decomposition AAS for Hg. Table 1 lists the digestion methods and instrumental analytical techniques used by the participants.

Results and discussion

Preliminary study of homogeneity

Using Pb as an example, the measurement results (Table 2) were treated as follows:

T, B, t', and G were computed, where: T = sum of each column; B = sum of each row; t' = mean of each column; and G = sum of $B_1 \ldots B_n$; b = number of replicate measurements from different aliquots of the solid material (3); and t = number of sub-samples (10)

The degree of freedom at 95% confidence level was calculated from:

$v = (b - 1)(t - 1)$, where v = the number of degrees of freedom

$v = 18$

The value of symbol q corresponding to t and v was found from the reference table given in ASTM 826-85.[12]

$q = 5.07$

The sum of squares due to the sub-samples, S_t, was calculated from

$S_t = [(T_1^2 + T_2^2 + \ldots T_t^2)/b] - (G^2/tb) = 341$

The sum of squares due to runs, S_b, was calculated from

$S_b = [(B_1^2 + B_2^2 + \ldots B_t^2)/t] - (G^2/tb) = 69$

Table 1 Digestion methods and instrumental analytical techniques used by participants in the inter-laboratory comparison exercise for elemental concentrations in NIMT/UOE/FM/001

Methodologies	
Total concentration	**Acid-extractable concentration**
Lab1: HNO_3–HBF_4 high pressure microwave autoclave, ICP-MS	**Lab1**: HNO_3 microwave-assisted, ICP-OES
Lab2: HNO_3–H_2O_2–H_2O–HF microwave-assisted, ICP-OES	**Lab2**: HNO_3 microwave-assisted, HR-ICP-MS
Lab3: HNO_3–HF pressure digestion, ICP-MS	**Lab3**: HNO_3 high-pressure ashing, ICP-MS, HG-AAS (for As)
Lab4: XRF	**Lab4**: HNO_3 microwave-assisted (USEPA Method 3051 Protocol), ICP-OES, GFAAS
Lab5: HNO_3–HF total digestion, ICP-OES	**Lab5**: aqua regia reflux digestion, ICP-OES
Lab6: HNO_3–HF microwave-assisted (USEPA Method 3052 Protocol), ICP-OES, GFAAS	**Lab6**: HNO_3 microwave-assisted (USEPA Method 3051 Protocol), GFAAS, ICP-OES; HNO_3/H_2SO_4 digestion @60 °C, 2 h, CVAAS (for Hg only)
Lab7: HNO_3–HF microwave-assisted (USEPA Method 3052 Protocol), ICP-MS	**Lab7**: aqua regia digestion RT 24 h, 100 °C, 1 h, ICP-MS, ICP-OES
Lab8: thermal decomposition AAS (for Hg only)	**Lab8**: aqua regia digestion @125 °C, 3 h, FAAS
Lab9: thermal decomposition AAS (for Hg only)	**Lab9**: HNO_3–$HClO_4$, heating, ICP-OES
	Lab10: HNO_3 microwave-assisted (USEPA Method 3051 Protocol), ICP-MS

The laboratory ID numbers in the total concentration column (and in Figs. 1 and 2) do not necessarily correspond to those in the acid-extractable concentration column (and in Figs. 3 and 4).

Table 2 Data for total Pb concentration (mg kg^{-1}) (dry-weight (105 °C) basis, *i.e.* corrected for moisture content of the air-dried peat) in the preliminary homogeneity testing of the candidate ombrotrophic peat (low ash) reference material

	Sub-sample numbers										
Replicate	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	Total
1	154	172	168	164	164	170	165	174	164	175	$B_1 = 1672$
2	175	188	169	163	164	169	163	172	163	180	$B_2 = 1705$
3	173	168	169	165	172	162	178	164	185	166	$B_3 = 1703$
Total	$T_1 = 501$	$T_2 = 528$	$T_3 = 506$	$T_4 = 493$	$T_5 = 500$	$T_6 = 501$	$T_7 = 507$	$T_8 = 511$	$T_9 = 512$	$T_{10} = 521$	$G = 5080$
Mean	$t'_1 = 167$	$t'_2 = 176$	$t'_3 = 169$	$t'_4 = 164$	$t'_5 = 167$	$t'_6 = 167$	$t'_7 = 169$	$t'_8 = 170$	$t'_9 = 171$	$t'_{10} = 174$	

The sum of squares of all the measurements in Table 2, $S_{average}$, was defined and calculated from

$$S_{average} = \left(\sum_{i=1}^{t}\right)\left(\sum_{j=1}^{b}\right) Y_{ij}^2 - (G^2/tb)$$

where Y_{ij} = individual values in Table 2.

$S_{average}$ = 1491

The symbol s was defined and calculated from

$$s = \sqrt{(S_{average} - S_b - S_t)/(b-1)(t-1)} = 7.8$$

The symbol w was defined and calculated from

$$w = qs/\sqrt{b} = 23$$

The maximum and minimum of the mean t' values in Table 2 are 176 and 164, respectively, so the maximum difference between any of the mean t' values in Table 2 is 12. As the absolute difference between any two mean values does not exceed w (=23), then there is strong evidence, at 95% confidence level, that the bulk material is homogeneous for Pb. The same treatment was applied to Al, Ca, Co, Cu, Fe, Mg, Mn, Ti, V, and Zn for which similar satisfactory evidence of homogeneity was obtained in each case.

Homogeneity testing

Analytical results for total Pb concentration, expressed in mg kg^{-1} on a dry-weight (at 105 °C) basis, are given in Table 3. Using Microsoft Excel®, Table 4 displays the associated ANOVA calculation (one-way layout), in which *SS* provides the sum of squares, *df* represents the associated degrees of freedom, and *MS* expresses mean squares, which form the basis for the computation of variation. The *P-value* gives the level for which the calculated F (F_{cal}) equals $F_{critical}$. From Table 4, where it can be seen that F_{cal} does not exceed $F_{critical}$, there is strong evidence, at the 95% confidence level, that the candidate peat bog reference material is homogeneous for total Pb concentration. The same treatment was applied to other elements of interest, in each case demonstrating the homogeneity of the candidate material. On the basis of these results, the material was considered to be homogeneous at the level of 0.25 g, the typical 30 °C air-dried weight taken for analysis.

Stability study

The ratios (R_T) of the mean values ($\bar{X}_T$) of five replicate measurements made for samples stored at +4 °C, +20 °C and +40 °C and the mean value ($\bar{X}_{-20\,°C}$) from the five determinations at −20 °C were calculated as:

$$R_T = \bar{X}_T/\bar{X}_{-20\,°C}$$

Table 4 Analysis of variance (ANOVA) for homogeneity testing of total Pb concentration (mg kg^{-1}) in the candidate ombrotrophic peat (low ash) reference material

Source of variation	*SS*	*df*	*MS*	F_{cal}	*P-value*	$F_{critical}$
Between bottles	575	15	38	1.559	0.142	1.992
Within bottles	787	32	25			
Total	1362	47				

The uncertainty U_T was obtained from the coefficient of variation (CV) of five measurements obtained at each temperature: $U_T = \left(CV_T^2 + CV_{-20\,°C}^2\right)^{1/2} R_T$

The R_T ratio should be 1 in the case of ideal stability but, as slight instability might be expected during long storage times, the value 1 should lie between $R_T - U_T$ and $R_T + U_T$. For greater than 98% of the measurements made for samples stored at these conditions, the values fell within $R_T \pm U_T$. It was concluded that there was no instability for a storage time of one year under these conditions. As the candidate material is stable under the storage condition of +40 °C for one year, it can be assumed that the material may be stable for up to two or three years under the storage condition of +20 °C or below. As a result of the stability testing, all of the elements determined were considered to be suitable for certification, provided that the material is stored at typical room temperature or under refrigeration.

Certification of concentration

The sets of results submitted by participants were assumed to be normally distributed, and analysed statistically[16,18] using Grubbs and Cochran's tests to detect outlying values. The Grubbs test[16,18] was used to detect outlying values in the population of individual results and in the population of laboratory means, while Cochran's test[16,18] was used to identify outlying values in the laboratory variances. A summary of the statistical evaluation is given in the certification report.

Using the certification of the total Pb concentration as an example, seven laboratories (1, 2, 3, 4, 5, 6, 7) submitted data for total Pb concentration. The Laboratory Means, standard deviation, and 95% confidence interval of the data from each laboratory are shown in Fig. 1a. The individual replicate results from each laboratory were tested for outliers by using Grubbs 1, Grubbs 2, and Grubbs 3 tests. One replicate from

Table 3 Data for total Pb concentration (mg kg^{-1}) (dry-weight (105 °C) basis, *i.e.* corrected for moisture content of the air-dried peat) in the homogeneity testing of the candidate ombrotrophic peat (low ash) reference material

	Concentration/mg kg^{-1}					
Sample	Replicate #1	Replicate #2	Replicate #3	Mean	Variance	*n*
#1	163	162	157	160	10.1	3
#2	162	160	161	161	0.8	3
#3	165	159	166	164	12.8	3
#4	165	158	159	161	17.1	3
#5	152	159	166	159	48.3	3
#6	159	166	161	162	10.2	3
#7	164	165	164	164	0.3	3
#8	165	162	165	164	3.2	3
#9	157	156	169	161	47.2	3
#10	164	163	161	163	2.6	3
#11	160	152	147	153	41.4	3
#12	158	154	148	153	27.6	3
#13	168	161	166	165	12.0	3
#14	162	165	166	164	4.2	3
#15	169	170	154	164	79.9	3
#16	154	154	169	159	75.8	3

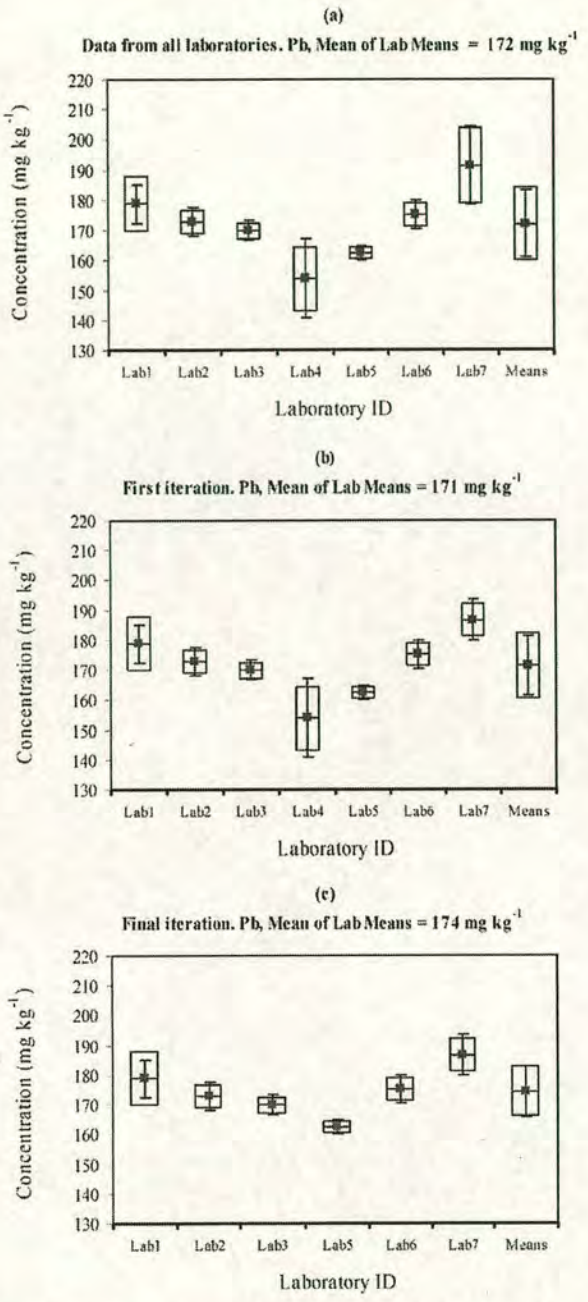

Fig. 1 Inter-laboratory comparison results for total Pb concentration (expressed as concentration, mg kg^{-1}, corrected for moisture content) of NIMT/UOE/FM/001: (a) data from all laboratories, (b) first iteration, (c) final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊏⊐).

Laboratory 7 was identified as a Grubbs 1 outlier. The outlier was then removed, with the resulting outcome for Laboratory 7 shown in Fig. 1b. The Laboratory Means of data from each laboratory were then tested for possible Grubbs 1, Grubbs 2, Grubbs 3, and Cochran's outliers. No Grubbs outlier was identified but it was decided to reject the Laboratory Mean from Laboratory 4 as a Cochran's outlier (variance outlying), evaluation of the data at this stage being displayed in Fig. 1c. Although the Laboratory Mean from Laboratory 1 could perhaps have been rejected as a Cochran's outlier (variance outlying), it was decided to retain it as the spread of results from the six laboratories was considered acceptable. The data processing was therefore stopped at this stage, with a mean Pb concentration of 174 mg kg^{-1}.

The sets of results accepted on technical and statistical grounds are presented in Figs. 2–4. Fig. 2 displays the calculated mean, standard deviation and 95% confidence interval (CI) of the accepted inter-laboratory comparison results for total Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn concentrations (expressed as concentration, mg kg^{-1}, corrected for moisture content), after the final iteration. For acid-extractable concentrations (expressed as concentration, mg kg^{-1}, corrected for moisture content), the calculated mean, standard deviation and 95% confidence interval of the accepted inter-laboratory comparison results after the final iteration are shown for As, Cd, Co, Cr, Cu, Mn, Ni, Pb V, and Zn in Fig. 3 and for Al, Fe, Mg and P in Fig. 4.

Calculation of uncertainty

Again using Pb as the example, the uncertainty of the value assigned to the total Pb concentration (174 mg kg^{-1}) of the ombrotrophic peat bog certified reference material was calculated according to a modification of the Guide on the Expression of Uncertainty in Measurement[19–24] (GUM), using the equation: $U_{CRM} = k\sqrt{u_{char}^2 + u_{bb}^2}$ where U_{CRM} = expanded uncertainty of the total Pb concentration of the peat bog certified reference material; k = coverage factor; u_{char} = uncertainty of the certified metal concentration in the ombrotrophic peat bog reference material; u_{bb} = uncertainty of the between-bottle inhomogeneity. The uncertainty of the instability (u_{stab}) was not included in view of the previously demonstrated stability and in accordance with criteria for the production of a quality control reference material.[16]

As we do not have the full uncertainty budget from the participants in the inter-laboratory comparison exercise, u_{char} can be calculated from the equation: $u_{char} = \frac{s}{\sqrt{l}}$ where s = standard deviation of laboratory means, *i.e.* 8 mg kg^{-1}; l = number of laboratories, *i.e.* 6. Therefore, u_{char} = 3.27 mg kg^{-1}, *i.e.* 1.88% of 174.

The value of u_{bb} can be estimated from ANOVA of the data from homogeneity testing as: $u_{bb} = \sqrt{\frac{MS_{among} - MS_{within}}{n}}$ where MS_{among} = mean square among units, *i.e.* 38; MS_{within} = mean square within units, *i.e.* 25; n = number of subsamples per unit, *i.e.* 3. Therefore, u_{bb} = 2 mg kg^{-1}, *i.e.* 1.29% of 174.

The expanded uncertainty of the value assigned to the total Pb concentration (174 mg kg^{-1}) in the ombrotrophic peat bog certified reference material can be calculated from: $U_{CRM} = ku_c$ where $u_c = \sqrt{u_{char}^2 + u_{bb}^2}$, *i.e.* 2.28%. Therefore, U_{CRM} (k = 2) = 4.56% of 174.

Therefore the certified value for total Pb concentration in the ombrotrophic peat (low ash) reference material NIMT/UOE/FM/001 is 174 ± 8 mg kg^{-1}.

Certified and information-only values

By applying the same treatment as for Pb to the other inter-laboratory comparison results, the certified values (coverage factor of 2) for all inorganic elements determined in the ombrotrophic peat (low ash) reference material NIMT/UOE/FM/001 were calculated and are displayed in Table 5. Where concentration data were not sufficient and considered too variable, the arithmetic means (±1 SD) are given as information-only values for some elements.

The acid-extractable concentrations of Cd, Pb, and Zn are similar to their corresponding total concentrations (Table 5), whereas the acid-extractable concentration of Cr and of some major elements such as Al, Na, and Ti are clearly lower than their corresponding total concentrations. This suggests that Cr and these major elements occur in matrices that cannot

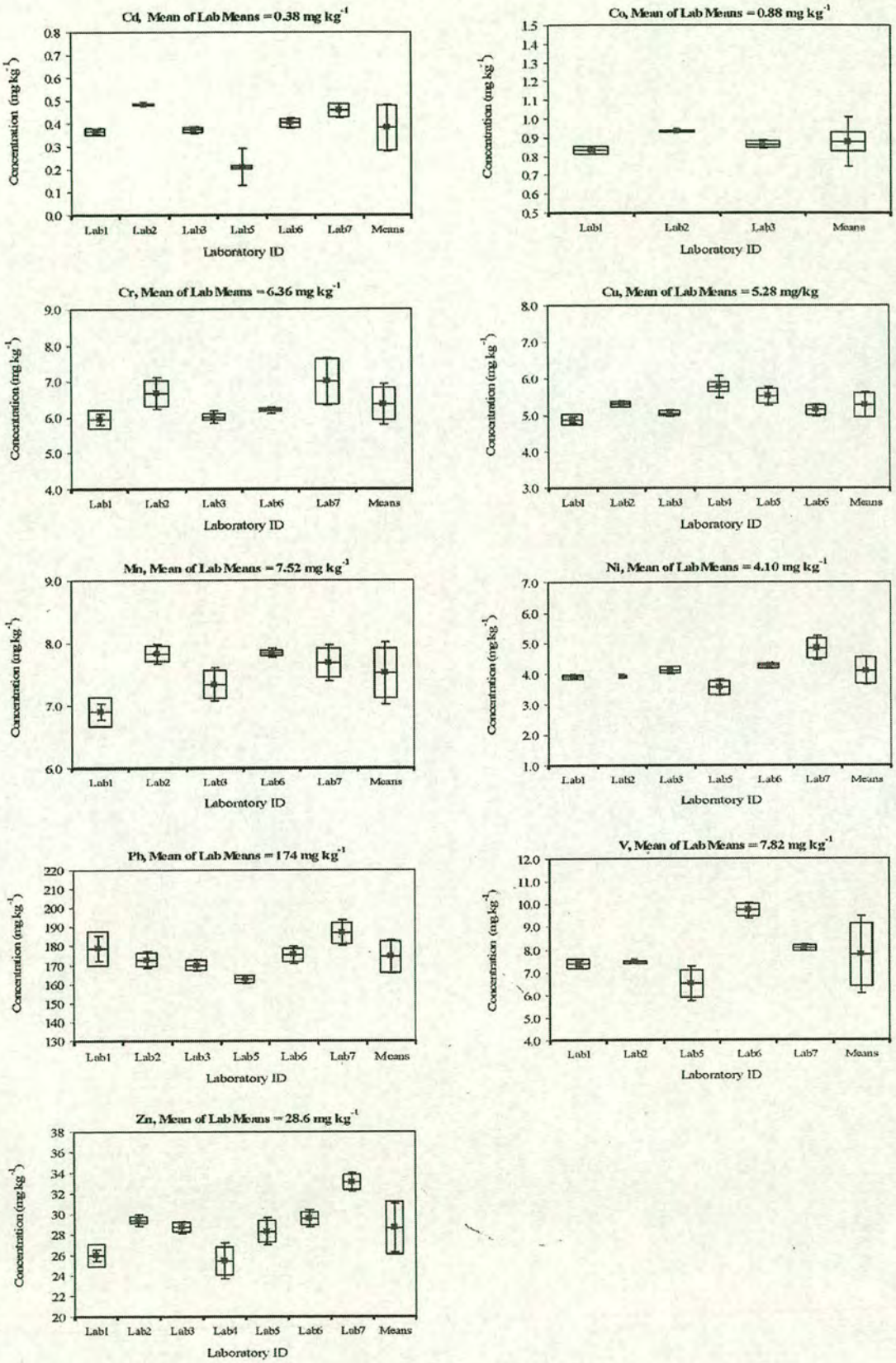

Fig. 2 Inter-laboratory comparison results for total Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn concentrations (expressed as concentration, mg kg^{-1}, corrected for moisture content) of NIMT/UOE/FM/001, after final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊥⊥).

be dissolved by conventional acid digestion methods. The employment of HF for wet digestion is needed in the study of Cr and some major elements. The variation of the acid-extractable results for some elements such as Al is probably a consequence of the range of digestion methods used by the participants.

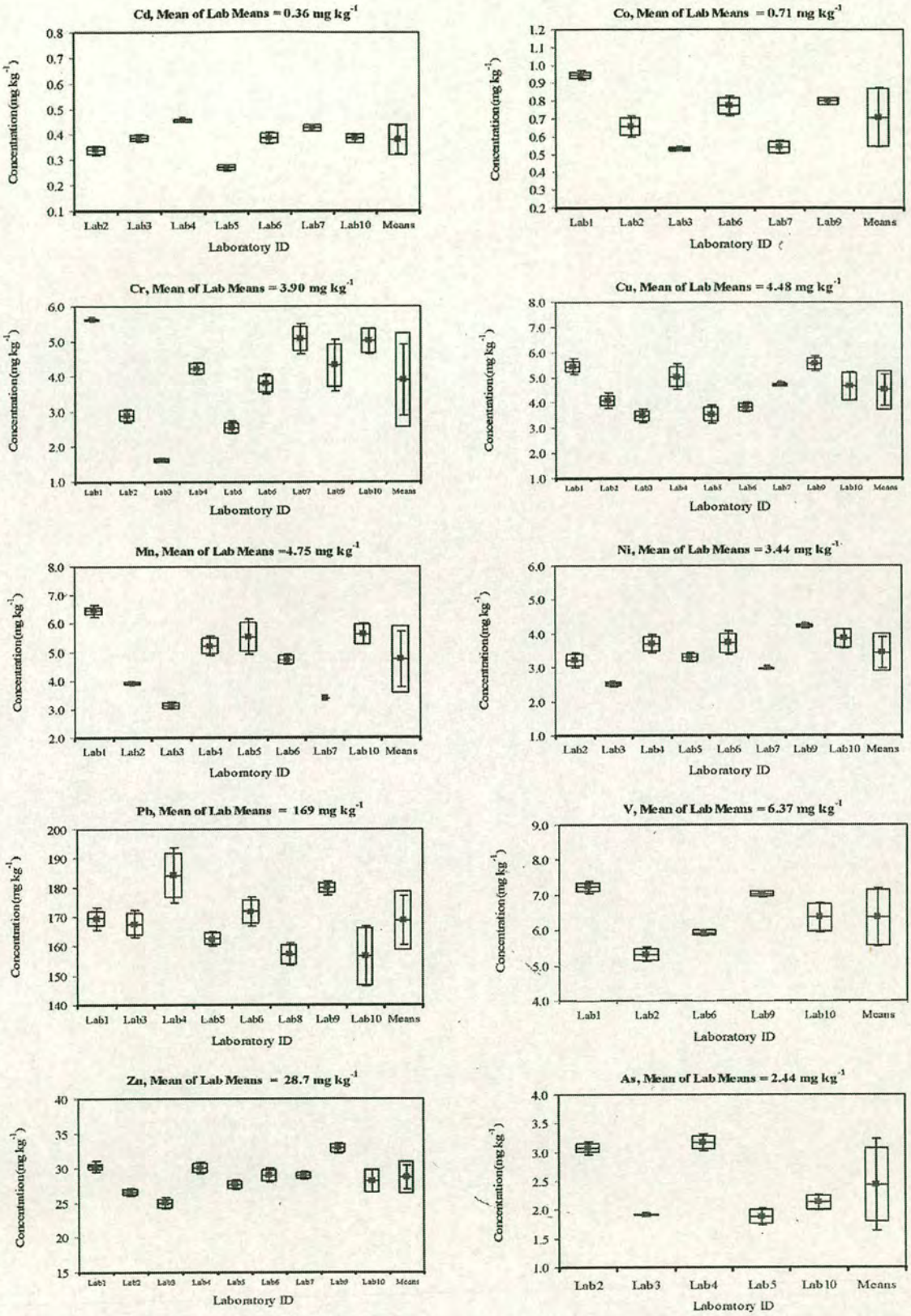

Fig. 3 Inter-laboratory comparison results for acid-extractable As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn concentrations (expressed as concentration, mg kg^{-1}, corrected for moisture content) of NIMT/UOE/FM/001, after final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊏⊐).

In addition to elemental concentration data, information on Pb isotopic composition was provided by three laboratories. Reported mean values of 1.1766 ± 0.0008, 1.1759 ± 0.0006, and 1.1765 ± 0.0003 yielded an overall information value of 1.1763 ± 0.0004 (±1 SD) for the $^{206}Pb/^{207}Pb$ ratio.

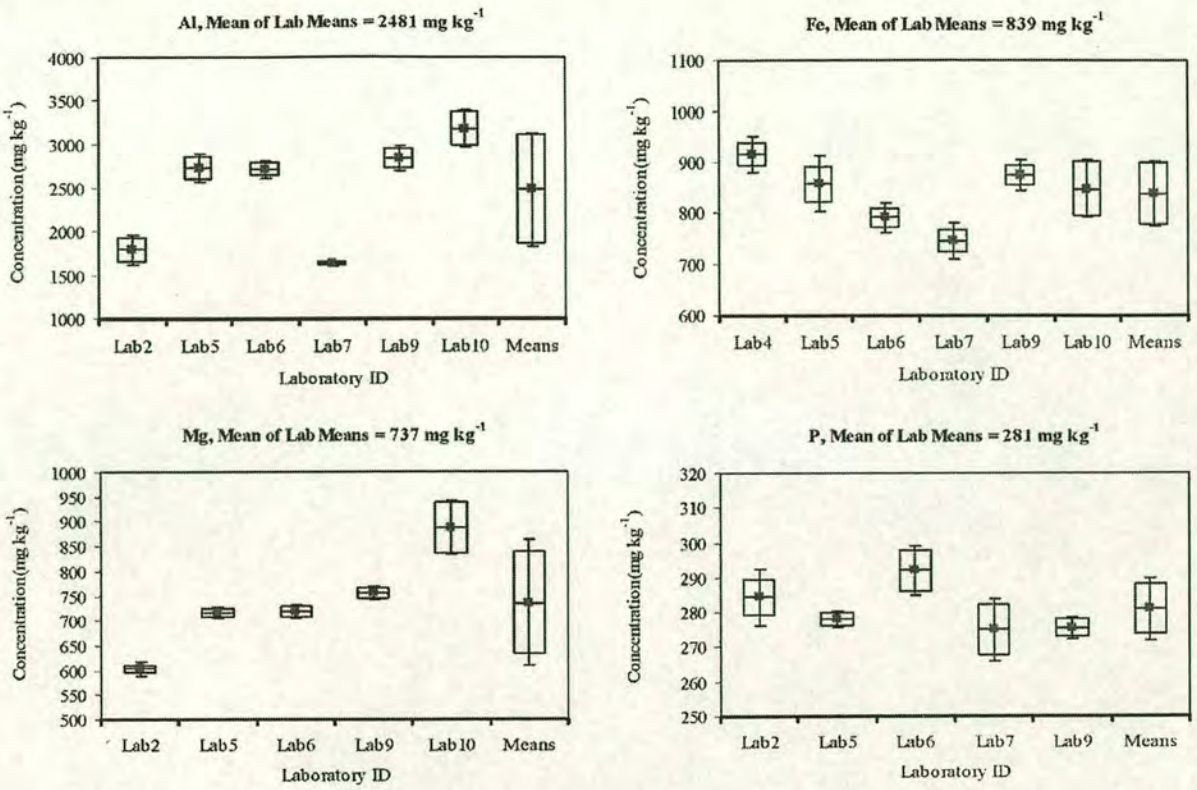

Fig. 4 Inter-laboratory comparison results for acid-extractable Al, Fe, Mg, and P concentrations (expressed as concentration, mg kg^{-1}, corrected for moisture content) of NIMT/UOE/FM/001, after final iteration, along with the calculated mean (■), standard deviation (□) and 95% confidence interval (⊏⊐).

Table 5 Certified values with uncertainties (coverage factor of 2) and information-only (italics) values [±1 SD ($n \leqslant 4$)] for the elemental concentration of the ombrotrophic peat (low ash) reference material NIMT/UOE/FM/001

	Certified values/mg kg^{-1}	
Element (x, y)[a]	Total concentration[b]	Acid-extractable concentration[b]
Cd (6, 8)	0.38 ± 0.08 (6)	0.36 ± 0.05 (7)
Co (4, 6)	0.88 ± 0.09 (3)	0.71 ± 0.13 (6)
Cr (6, 9)	6.36 ± 0.44 (5)	3.90 ± 0.90 (9)
Cu (7, 10)	5.28 ± 1.04 (6)	4.48 ± 0.73 (9)
Fe (4, 8)	*921 ± 84 (4)*	839 ± 54 (6)
Mn (6, 8)	7.52 ± 0.41 (5)	4.74 ± 0.87 (8)
Ni (7, 10)	4.10 ± 0.37 (6)	3.44 ± 0.40 (8)
Pb (7, 10)	174 ± 8 (6)	169 ± 8 (8)
V (5, 6)	7.82 ± 1.08 (5)	6.37 ± 0.73 (5)
Zn (7, 10)	28.6 ± 1.9 (7)	28.7 ± 1.6 (9)
As (4, 5)	*2.44 ± 0.55 (3)*	2.44 ± 0.58 (5)
Hg (2, 2)	*0.169 ± 0.007 (2)*	*0.164 ± 0.020 (2)*
Al (3, 6)	*3692 ± 347 (3)*	2481 ± 514 (6)
Ca (3, 4)	*683 ± 198 (3)*	*763 ± 172 (4)*
Mg (2, 5)	*582 ± 168 (2)*	737 ± 95 (5)
Na (3, 3)	*817 ± 307 (3)*	*229 ± 78 (3)*
P (2, 5)	*265 ± 8 (2)*	281 ± 7 (5)
Ti (3, 3)	*357 ± 18 (3)*	*110 ± 11(3)*

[a] x and y indicate the number of laboratories that submitted results for total and acid-extractable elemental concentrations, respectively. [b] Under total and acid-extractable concentration, the number in brackets indicates the number of accepted laboratory results used in the certification exercise for each element.

Applicability and availability

Although this ombrotrophic peat (low ash) reference material has been developed specifically for use in the analysis of ombrotrophic peat, it may also be of some value in the analysis of minerotrophic peat. Enquiries concerning the availability of the reference material NIMT/UOE/FM/001 for use by laboratories should be made to Dr. J. G. Farmer, University of Edinburgh, from whom instructions for use can also be obtained.

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